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The non-isothermal crystallization kinetics of Sb_2S_3 in the $(GeS_2)_{0.2}(Sb_2S_3)_{0.8}$ glass

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Abstract

The crystallization of Sb_2S_3 in the $(GeS_2)_{0.2}(Sb_2S_3)_{0.8}$ glass was studied under non-isothermal conditions. The influence of the sample form on crystallization was studied using bulk sample and two fractions of powder sample. The crystallization process of the sample in the form of powder was described using autocatalytic model, the crystallization of the bulk sample was described using nucleation-growth model. The parameters of both the models were determined.

Keywords: Crystallization kinetics; Chalcogenide glass; Nucleation-growth model; Autocatalytic model

1. Introduction

Some papers dealing with the differential scanning calorimeter (DSC) study of the Ge-Sb-S glass can be found in literature. Not only the glass transition area [1] and physical properties [2] are studied but also the crystallization of Ge-Sb-S glass is in the center of interest [3]. Probably the most results were published about the crystallization kinetics of $(GeS_2)_{0.3}(Sb_2S_3)_{0.7}$ composition. The non-isothermal kinetics was studied on bulk and powders too. The non-isothermal crystallization of powder was described by autocatalytical model AC(M, N) [4], M and N are parameters of this model. The non-isothermal crystallization of bulk sample was described by nucleation-growth model JMA(m) for the parameter $m = 2$ [5] or $m = 3$ [6]. The crystallization of $(GeS_2)_{0.3}(Sb_2S_3)_{0.7}$ glass in the form of bulk under isothermal conditions was described by JMA model with the parameter $m = 2$ [7] but the isothermal crystallization of sample in the form of powder can not be described within JMA model [6].

As is seen there is some uncertainty in published description of non-isothermal bulk crystallization of $(GeS_2)_{0.3}(Sb_2S_3)_{0.7}$ glass. In this paper, the crystallization of Sb_2S_3 in slightly different composition—$(GeS_2)_{0.2}(Sb_2S_3)_{0.8}$ glass is studied under non-isothermal conditions for samples in the form of bulk and powder. The DSC is used for these studies. The measured heat flow Φ can be described by the kinetic equation [8]:

$$\Phi = \Delta H A \exp\left(\frac{-E}{RT}\right) f(\alpha) \tag{1}$$

where ΔH is the crystallization enthalpy; A, the pre-exponential factor; E, the apparent activation energy; R, a gas constant and T, the temperature. The function $f(\alpha)$ is an analytical expression of the kinetic model. One of the most widely used kinetic models is theoretical one-parameter nucleation-growth model JMA(m) [8]:

$$f(\alpha) = m(1-\alpha)[-\ln(1-\alpha)]^{1-(1/m)} \tag{2}$$

where α is the conversion and the kinetic exponent m reflects nucleation rate and crystal morphology. The Eq. (2) was derived for isothermal conditions but Henderson [9] showed that the validity of this model can be extended to non-isothermal conditions under two assumptions - first the growth rate of a new phase is controlled only by temperature and is independent of time and second the nucleation process takes place during the early stages of the transformation and

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become negligible during the crystal growth. The empirical two-parameter autocatalytic model AC(M, N) is also used for description of kinetics processes [8]:

$$f(\alpha) = \alpha^M (1-\alpha)^N \tag{3}$$

The value of parameter M is limited to (0, 1) interval. Parameters M and N of this model have not clear physical meaning yet.

Very simple way how to test the applicability of commonly used models is calculation of function $y(\alpha)$ and $z(\alpha)$ [6]. In non-isothermal conditions the functions are defined as:

$$y(\alpha) \approx \Phi \exp\left(\frac{E}{RT}\right) \tag{4}$$

$$z(\alpha) \approx \Phi T^2 \tag{5}$$

These functions $y(\alpha)$ and $z(\alpha)$ are normalized within the $\langle 0, 1 \rangle$ range. The value of conversion corresponding to the maximum of $z(\alpha)$ function α_p^∞ is constant (0.632) for JMA model. When the value of conversion corresponding to the maximum of $y(\alpha)$ function α_M is lower than α_p^∞ the studied process can be described by JMA model (when the condition for α_p^∞ is fulfilled) or by AC model [10].

In this work, first the applicability of commonly used models for description of non-isothermal Sb_2S_3 crystallization in $(GeS_2)_{0.2}(Sb_2S_3)_{0.8}$ glass is tested and then the parameters of these models are calculated.

2. Experimental

The glass $(GeS_2)_{0.2}(Sb_2S_3)_{0.8}$ was prepared by conventional method from pure elements (5N). Weighted elements in evacuated quartz ampoule were melted and homogenized at 950 °C for 20 h. The melt was quenched in ice-water and the ingot of glass arose. The amorphous nature of prepared glass was confirmed by X-ray diffraction. Two types of samples were prepared from the glass ingot to be able to study the surface influence on crystallization process of Sb_2S_3 in the glass $(GeS_2)_{0.2}(Sb_2S_3)_{0.8}$. The bulk samples were in the form of both sides polished thin plates. The crushed glass in the form of powder was divided according to the particle size into two fractions: 250–125 μm and 125–50 μm. The crystallization process was studied under non-isothermal conditions using DSC Pyris 1 (Perkin-Elmer). The instrument was previously calibrated with six standards (Hg, Ga, In, Sn, Pb and Zn) for heating rate extrapolated to 0 K/min. The 10 mg of the powder sample and ca. 30 mg of the bulk sample, respectively, in the standard aluminium sample pans were measured. The non-isothermal experiments were done in the temperature range 50–400 °C with heating rate 5–30 K/min.

In the case of sample in the form of powder the attention must be paid to "ageing of prepared powder" during experimental work. When the bulk is crushed into powder and this powder is used for crystallization experiments after longer time the kinetic behaviour as well as the enthalpy change may be different. This usually indicates necessity to prepare freshly crushed powder sample.

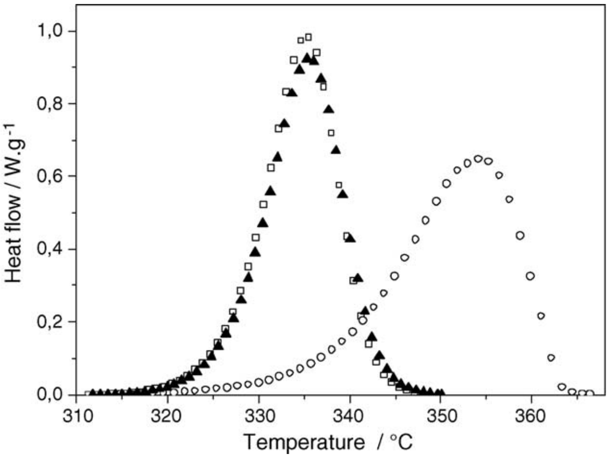

Fig. 1. Non-isothermal crystallization of Sb_2S_3 in $(GeS_2)_{0.2}(Sb_2S_3)_{0.8}$ glass in the form of (○) bulk, (▲) powder with 250–125 μm and (□) powder with 125–50 μm particle size for heating rate 10 K/min.

3. Results

This work is focused on comparison of bulk and powder non-isothermal crystallization kinetics of Sb_2S_3 in the $(GeS_2)_{0.2}(Sb_2S_3)_{0.8}$ glass. Also the difference, if there is any in crystallization behaviour of powders with different particle size is studied.

During the non-isothermal experiments the glass transition was observed and the value of the glass transition temperature was determined in the range 230–243 °C for all studied types of sample for heating rate 5–30 K/min. The temperature range of non-isothermal crystallization effects of bulk sample is 309–393 °C for heating rates 5–30 K/min. The crystallization of both fractions of powdered samples is shifted towards lower temperatures 303–370 °C for used heating rates. Also the shape of crystallization peak of bulk and powdered samples is different. Crystallization peaks of bulk and both powdered fractions for non-isothermal experiment with heating rate 10 K/min are shown in Fig. 1. The crystallization peak of powdered fraction 250–125 μm is shifted a bit toward higher temperature and is lower comparing to fraction 125–50 μm for all used heating rates. The crystallization process of powder sample is shifted toward lower temperature compare to bulk crystallization. This is probably due to non-negligible surface nucleation in the case of powder sample.

4. Discussion

First and the most important step in kinetic analysis of DSC data is to determine the apparent activation energy. In the case of non-isothermal experiments, the temperature cor-

Table 1
Activation energy of crystallization E (kJ/mol) of Sb_2S_3 in the $(GeS_2)_{0.2}(Sb_2S_3)_{0.8}$ glass determined using Kissinger, Ozawa and isoconversional method

Sample	Kissinger method	Ozawa method	Isoconversional method
Bulk	178 ± 9	179 ± 8	180 ± 4
Powder 250–125 μm	222 ± 6	221 ± 5	216 ± 7
Powder 125–50 μm	227 ± 1	226 ± 3	227 ± 8

Table 2
Crystallization enthalpy ΔH and conversion α_M and α_p^∞ corresponding to the maximum of function $y(\alpha)$, $z(\alpha)$ for all types of $(GeS_2)_{0.2}(Sb_2S_3)_{0.8}$ glass samples studied

Sample	ΔH (J/g)	α_M	α_p^∞
Bulk	−65	0.43	0.63
Powder 250–125 μm	−61	0.44	0.55
Powder 125–50 μm	−61	0.46	0.57

responds to the maximum of crystallization peak T_p is usually used to calculate E according to Kissinger [11] or Ozawa [12]. Isoconversional method, where the value for the same conversion $\ln \Phi_\alpha$ versus $1/T_\alpha$ gives the slope $-E/R$, is applicable for non-isothermal data too [13]. Table 1 shows the values of apparent activation energy of non-isothermal crystallization determined using all three methods mentioned above. The plots corresponding to Ozawa method for all studied samples are shown in Fig. 2. The values of E calculated using all three methods are similar for each type of sample. The value of E of bulk sample is lower than for the samples in the form of powder. There is no significant difference in E between two fractions of powder at least within the error limits presented in Table 1. The values of apparent activation energy of crystallization determined by Ozawa method were used for calculations described below.

The second step consists in determination of the appropriate kinetic model. This can be done by using the function $y(\alpha)$, $z(\alpha)$ and the values of conversion corresponding to their maximum. The experimental data can be simply transformed into the functions $y(\alpha)$ and $z(\alpha)$ according the Eqs. (4) and (5). In Table 2, there are values of conversion corresponding to the maximum of $y(\alpha)$ and $z(\alpha)$ function, α_M and α_p^∞, respectively. The error limit was found to be 0.02 (standard deviation of values for all used heating rates) for non-isothermal crystallization of Sb_2S_3. As is seen the crystallization experiments of the glass in the form of bulk fulfil the α_p^∞ condition of applicability of JMA model. The crystallization process of samples in the form of powder can not be correctly described by JMA model but the AC model can be used instead. The illustration of $y(\alpha)$ and $z(\alpha)$ function for non-isothermal data is in Fig. 3.

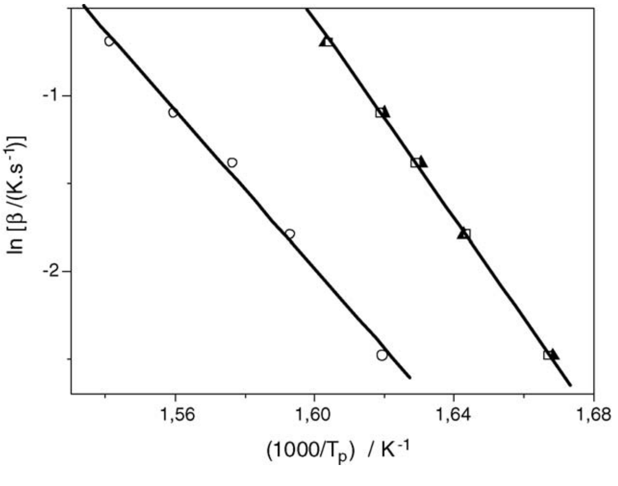

Fig. 2. Determination of activation energy according to the Ozawa method for Sb_2S_3 crystallization in the sample form of (◯) bulk, (▲) powder with 250–125 μm and (□) powder with 125–50 μm particle size.

The information about crystallization behaviour of $(GeS_2)_{0.2}(Sb_2S_3)_{0.8}$ glass is in Table 2 completed with the values of crystallization enthalpy of Sb_2S_3. The error limit of crystallization heat is 1.5 J/g. The crystallization heat of all studied types of sample increases with heating rate (within the error limit). The value of ΔH for bulk sample is higher

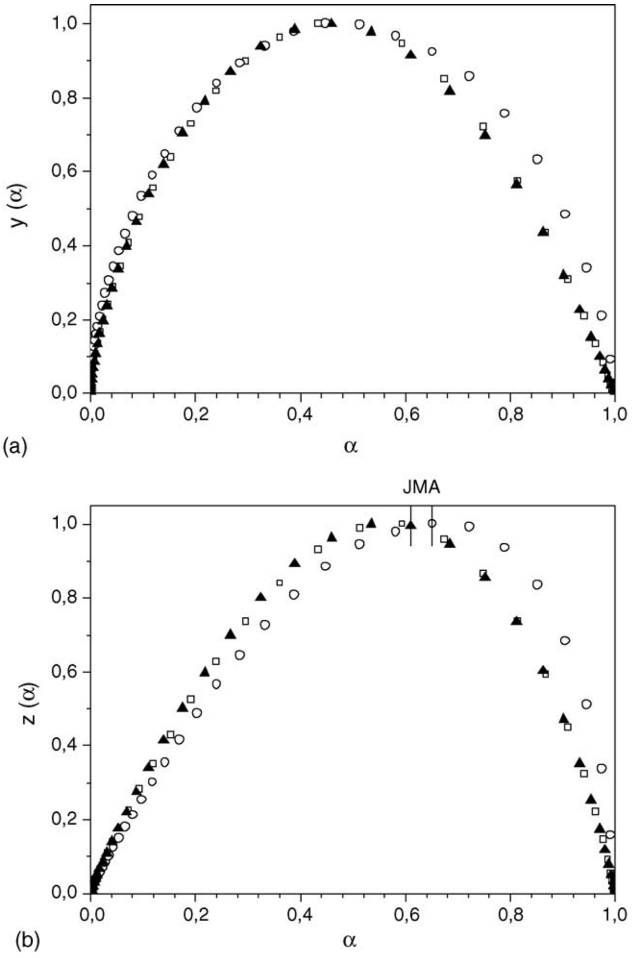

Fig. 3. Normalized $y(\alpha)$ and $z(\alpha)$ function obtained by transformation of non-isothermal data for the crystallization of Sb_2S_3 in $(GeS_2)_{0.2}(Sb_2S_3)_{0.8}$ glass (Fig. 1). The form of sample is shown by points: (◯) bulk, (▲) powder with 250–125 μm and (□) powder with 125–50 μm particle size. Solid lines show the typical interval of α_p^∞ values for the JMA model (0.63 ± 0.02).

compare to the powder samples because the crystallization process in bulk is observed at higher temperature.

4.1. Application of autocatalytic model AC(M, N)

The crystallization process of $(GeS_2)_{0.2}(Sb_2S_3)_{0.8}$ glass in the form of powder can be described using empirical AC(M, N) model. The parameters of this model can be determined in a simple way. The conversion corresponds to the maximum of $y(\alpha)$ function can be used to calculate the quotient of parameters M and N [14]:

$$\frac{M}{N} = \frac{\alpha_M}{1-\alpha_M} \tag{6}$$

When the activation energy of crystallization is known and the quotient of parameters M and N is calculated according the previous equation all parameters can be determined from the dependence [14]:

$$\ln\left[\Phi \exp\left(\frac{E}{RT}\right)\right] = \ln(\Delta HA) + N \ln\left[\alpha^{M/N}(1-\alpha)\right] \tag{7}$$

This equation is valid in the interval $0.2 < \alpha < 0.8$. The parameter N is determined directly from the slope of this dependence and then the parameter M using Eq. (6). Also the pre-exponential factor A can be calculated from the section of the dependence (7) because the ΔH value is known (Table 2). In Table 3 are summarized the values of parameters of AC model and the pre-exponential factor describing the non-isothermal crystallization kinetics of Sb_2S_3 in the $(GeS_2)_{0.2}(Sb_2S_3)_{0.8}$ glass. The AC model describes the crystallization in both fractions of powdered sample under non-isothermal conditions very well. The comparison of experimental data and calculated lines is illustrated in Fig. 4 for powder sample with 250–125 μm particle size. Within the error limits the values of parameter M and N are the same for both the powder fractions. Nevertheless, in the case of parameters describing the 125–50 μm powder the error limits are higher. The possible interpretation of this higher error limits is that the powder of size 125–50 μm is slightly “inhomogeneous” from the crystallization kinetics point of view. The parameters of AC model for bulk sample are given in Table 3 for illustration purpose only. The crystallization of bulk sample will be discussed in the next section. The parameter M and N of AC model are almost two times higher for the powder samples comparing to bulk, the different value of A is partly influenced by difference in ΔH for bulk and powder samples.

Table 3
Parameters of AC(M, N) model describing the Sb_2S_3 crystallization in the $(GeS_2)_{0.2}(Sb_2S_3)_{0.8}$ glass

Sample	M	N	ln (A/s)
Powder 125–50 μm	0.85 ± 0.11	1.02 ± 0.11	42.0 ± 0.1
Powder 250–125 μm	0.79 ± 0.04	1.00 ± 0.02	40.9 ± 0.1
Bulk	0.45 ± 0.03	0.58 ± 0.03	30.5 ± 0.1

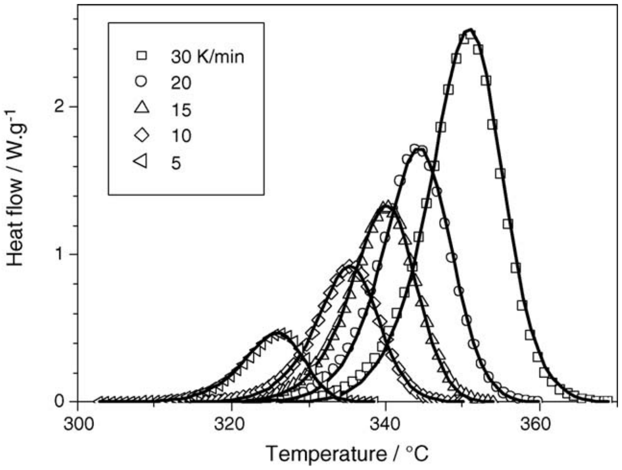

Fig. 4. Non-isothermal crystallization of Sb_2S_3 in $(GeS_2)_{0.2}(Sb_2S_3)_{0.8}$ powder sample with 250–125 μm particle size for different heating rates compared with the calculated dependences (line) using AC model and parameters given in Table 3.

4.2. Application of nucleation-growth model JMA (m)

The JMA model can be used to describe the crystallization behaviour of the bulk sample of $(GeS_2)_{0.2}(Sb_2S_3)_{0.8}$ composition. There are two ways how to determine the parameter m of JMA model. The value of conversion α_M corresponding to the maximum of $y(\alpha)$ function can be used [15] and the parameter m is calculated as $m = [1 + \ln(1 - \alpha_M)]^{-1}$. Using the α_M value for bulk sample given in Table 2 the parameter of JMA model is 2.3 ± 0.2. That is not so far from $m \cong 2$ (within the limits of experimental errors). The comparison of experimental data and the calculated temperature dependence of heat flow using JMA model with $m = 2$ and the best fit value of A is in Fig. 5. It is seen that the calculated lines do not correspond very well with the experimental data.

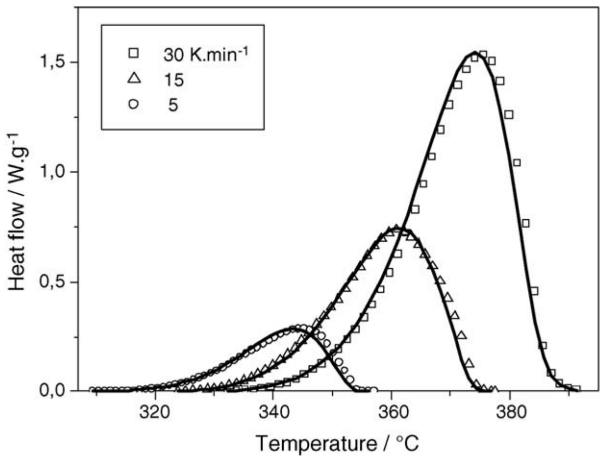

Fig. 5. Non-isothermal crystallization of Sb_2S_3 in $(GeS_2)_{0.2}(Sb_2S_3)_{0.8}$ bulk for different heating rates compared with the calculated dependences (line) for JMA model with $m = 2$ and $\ln(A/s) = 47.2$.

Double logarithm function of conversion can be used to determine the parameter of JMA model too [8]:

$$\frac{\mathrm{d}\ln[-\ln(1-\alpha)]}{\mathrm{d}(1/T)} \cong \frac{mE}{R} \tag{8}$$

The linear dependence of this equation is often used as a method to test the applicability of the JMA model. The double logarithm function is not very sensitive and the linear dependence can be observed even if the conditions of JMA model applicability are not fulfilled. The parameter m determined according to the Eq. (8) for Sb_2S_3 crystallization in bulk sample is 2.8 ± 0.2. Based on this method of calculation the parameter of JMA model can be used as $m \cong 3$. The comparison of calculated lines for $m = 3$ with the experimental data gives similar result as in Fig. 5 for $m = 2$.

Using both the methods of parameter m determination the same uncertainty for $(GeS_2)_{0.2}(Sb_2S_3)_{0.8}$ composition can be observed as in the non-isothermal crystallization of Sb_2S_3 in the $(GeS_2)_{0.3}(Sb_2S_3)_{0.7}$ glass [5,6]. The isothermal crystallization of Sb_2S_3 in bulk sample of $(GeS_2)_{0.3}(Sb_2S_3)_{0.7}$ glass can be described using JMA model with $m = 2$ [7]. The same result was obtained for isothermal crystallization of bulk sample of $(GeS_2)_{0.2}(Sb_2S_3)_{0.8}$ glass [16]. In both these compositions the non-isothermal crystallization can be also described using JMA model, but the parameter m is between 2 and 3. This range of parameter m and difference with respect to the isothermal crystallization mean that the crystallization under non-isothermal condition is more complicated process compared to isothermal crystallization.

5. Conclusions

The crystallization of Sb_2S_3 in the $(GeS_2)_{0.2}(Sb_2S_3)_{0.8}$ glass was studied under non-isothermal conditions. The influence of surface activated nucleation on crystallization kinetics was studied using two types of sample - bulk and powder divided into two fractions according to the particle size. The activation energy of crystallization determines using Kissinger, Ozawa and isoconversional method is the same for all these methods for each type of studied samples. The value of E for bulk sample is lower than for the powder sample, there is no significant difference in E for studied fractions of the powder. The appropriate model describing the crystallization process was chosen on the bases of $y(\alpha)$ and $z(\alpha)$ functions. The crystallization of the powder fractions is described using autocatalytic model, the determined parameters M and N are not very different for both the fractions. The non-isothermal crystallization in bulk sample is described using JMA model with the parameter m between 2 and 3. This uncertainty in parameter m determination reflects complicated character of crystallization process under non-isothermal conditions.

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References

[1] T. Asami, K. Matsuishi, S. Onari, T. Arai, J. Non-Cryst. Solids 226 (1998) 92–98.

[2] H. Tichá, L. Tichý, N. Ryšavá, A. Tříska, J. Non-Cryst. Solids 74 (1985) 37–46.

[3] X. Zhang, M.A. Hongli, J. Lucas, J. Non-Cryst. Solids 337 (2004) 130–135.

[4] J. Málek, E. Černošková, R. Švejka, J. Šesták, G. Van der Plaats, Thermochim. Acta 280/281 (1996) 353–361.

[5] N. Ryšavá, L. Tichý, Č. Bárta, A. Tříska, H. Tichá, Phys. Status Solidi 87 (1985) K13–K17.

[6] J. Málek, Thermochim. Acta 355 (2000) 239–253.

[7] N. Rysavá, T. Spasov, L. Tichý, J. Therm. Anal. 32 (1987) 1015–1021.

[8] J. Šesták, Thermophysical Properties of Solids, Their Measurements and Theoretical Analysis, Elsevier, Amsterdam, 1984.

[9] D.W. Henderson, J. Non-Cryst. Solids 30 (1979) 301–315.

[10] J. Málek, Thermochim. Acta 200 (1992) 257–269.

[11] H.E. Kissinger, Anal. Chem. 29 (1957) 1702–1706.

[12] T. Ozawa, J. Therm. Anal. 2 (1970) 301–324.

[13] H.L. Friedman, J. Polym. Sci. C6 (1964) 183–195.

[14] J. Málek, Sci. Papers Univ. Pardubice 2 (1996) 177–208.

[15] J. Málek, Thermochim. Acta 138 (1989) 337–346.

[16] Unpublished results.