

BINARY SYSTEM NITROCELLULOSE FROM LINTERS + *sym*-DIETHYLDIPHENYLUREA

Thermal analysis of phase transition and pore structure

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Three different nitrocellulose (NC) samples produced from linters were investigated. DSC studies on the NC+*sym*-diethyldiphenylurea (C1) mixtures were carried out. The influence of storage time on their pore structures was examined using thermoporometry. The results led to conclusion that large pores are multiples of small ones. The parameter n was used to characterize the number of C1 molecules equivalent to NC ring. Its value for short storage time was about 9 but for longer time reached the value of 3. The influence of thermal history on the phase transition and porosity of the different nitrocellulose samples was different.

Keywords: diethyldiphenylurea, DSC, melting enthalpy, nitrocellulose, pore structure, thermoporometry

Introduction

Nitrocellulose (NC) is a chemically modified material obtained from nitration of naturally occurring polymer cellulose. The porous structure of cellulose is formed by natural processes and different industrial modifications. When it is treated with nitrating acid and nearly all of their hydroxyl groups are esterified, no significant degradation of original molecular structure is observed. The porosity of NC is important during manufacturing of the end products.

The cotton fibre assumes shape of a tube which consists of a cuticle that envelopes it, a cell wall that is made up of primary (P, outer) and secondary (S₁, S₂, inner) layers, and a residual protoplasm called the lumen. The thickness of outer layer cuticle reaches 0.1 μm. The cellulose chains in the secondary wall are aggregated to form fibrils that are laid down in series of concentric growth rings or lamellas [1]. The thickness of individual layers (S₁, S₂) in the secondary wall ranges from 50 to 250 nm. They are built from elementary fibrils that associate into aggregates to form microfibrils and larger aggregates called macrofibrils. Different papers present different dimensions for these structures, but typically the elementary fibrils measure 3.5–10 nm, the microfibrils 10–40 nm, and the macrofibrils are 60–300 nm wide. The empty spaces in secondary wall form pores of different diameter e.g. intrafibril (about 10 nm) and intramolecular (about 1–3 nm).

During the industrial production of NC linters are nitrated [2]. Wickholm [3] reported that using different measuring techniques the same thickness of microfibrils about 7.1 nm in linters were evaluated.

Nitrocellulose (NC, cellulose nitrate) processing requires addition of the low molecular compounds. These compounds can act as plasticizers and solvents enabling low temperature treatment of nitrocellulose masses and stabilizers protecting the polymer durability. Symmetric diethyldiphenylurea (C1, centralite I) is applied in the nitrocellulose processing technology as a plasticizer and stabiliser. There is very little information in the literature on the way, which it interacts with NC [4–6]. It is known that C1 forms strong hydrogen bonds with hydroxyl groups of NC [5, 6]. Mikhailov *et al.* [5] proves on the basis of IR spectra of NC–C1 films, that the molecular complexes can appear in this system.

The porous structure of materials can be investigated by means of thermoporometry, method based on the depression of melting temperature of substances filling the pores [7]. Analysis can be carried out by differential scanning calorimetry (DSC) [4, 8], which allows to estimate pores radii in the range of 2–150 nm. This method is especially useful for investigation of swelling materials [9]. The precondition of reliable DSC measurements is complete filling of pores by liquid phase that undergoes the phase transition. Previously we investigated the binary mixtures of NC+water [4], NC+C1 [10–12], NC+2,6-dinitrotoluene [13] and NC+2,4-dinitrotoluene [14]. The nitrocellulose applied in these studies was produced in the process of nitrating cellulose obtained from tree pulp. In the latest researches another properties of products obtained from NC were studied e.g. relaxation transitions of gunpowder [15] and compatibility of 1,3,3-trinitroazetidine with energetic components [16].

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The aim of this work was to determine the structures of NC obtained from linters, formed during migration of C1 into the existing fibre structures. In structural studies we analysed the liquid-crystal equilibrium of C1 that acts as plasticizer and stabilizer.

Experimental

Materials

Three kinds of nitrocellulose (NC) produced from linters were used in this study. They were obtained from Allachem a.s. Plant – division of Synthesia Pardubice (Czech Republic). Bulk samples of nitrocellulose were taken from different batches. The structural parameters of NC samples were evaluated with the BJH adsorption-desorption method. The mean surface (A), mean pore volume (V) and pore diameter are summarized in Table 1. The nitrogen adsorption-desorption measurements were carried out on Micrometrics ASAP 2405 analyser. Two additional parameters provided by producer – nitrogen content and viscosity of 1% solutions of NC samples in acetone are also presented in Table 1.

S-diethyldiphenylurea (C1) was crystallized three times from ethanol. Its purity was determined by the cryometric method and was equal 99.9 mol%. Samples of C1 were analysed by DSC method, in order to determine the following thermochemical parameters: melting temperature was $T_m^0=343.3$ K, melting enthalpy was $\Delta H_{ml}^0=110$ J g⁻¹, glass transition temperature at heating rate $\beta=20$ K min⁻¹ was $T_{gC1}=225.8$ K and heat capacity change during the glass transition was $\Delta c_p^0=0.629$ J g⁻¹ K⁻¹.

Method

Differential scanning calorimetry (DSC)

Nitrocellulose samples were mixed with appropriate amounts of powdered C1 to give mixtures with similar mass fractions of NC $x_{wNC}=0.03$. Samples with masses of about 20–40 mg were taken from these mixtures and pressed under a pressure of about 0.5 GPa into tablets with the dimensions and shape of aluminium calorimetric pans. The samples were sealed hermetically in pans under reduced pressure to about 1.3 kPa. The abbreviations used by us for mixtures of NC and C1 are the same as for NC in Table 1. It is assumed that

during the first DSC measurements C1 melts and its molecules start to penetrate into NC structures. The melting process of C1 in prepared tablets was carried out with heating rate $\beta=2$ K min⁻¹ from room temperature to 380 K, then they were cooled on the surface of ice to crystallize C1. The study of pore structure of NC is based on thermoporometry. Measurements were performed on Perkin-Elmer Pyris DSC 1 microcalorimeter using three different methods (I, II and III).

In method I the temperature range of 298–380 K and heating rate $\beta=2$ K min⁻¹ was applied during experiments. The parameters of melting of C1 in confined spaces (pores) and in unconfined spaces (bulk melting) were used for evaluating of pore radii. In method II temperature ranged from 173 to 380 K and heating rate $\beta=20$ K min⁻¹ was set. In method III experiments were carried out in fixed thermal cycles. In the first step samples were heated from 173 to 380 K and with heating rate $\beta=20$ K min⁻¹, next the cooling to 173 K with rate $\beta=200$ K min⁻¹ was applied. In the established temperature 173 K samples were kept 60 s and the following heating with rate 20 K min⁻¹ to 380 K was performed. Methods II and III were used for the investigation of phase changes, first of all for glass transition phenomenon. Successive DSC measurements were carried out for samples stored in room temperature in hermetic pans for specified periods of time (from hours to 36 months). Experiments performed with high heating rate (20 K min⁻¹) were no useful for determination of pore size distribution because under this condition melting process undergoes in the thermodynamically unstable system. The thermodynamic equilibrium of experiments is a principal condition for applying of thermoporometry. Therefore method I was used for determination of pore sizes. The decrease of melting temperature of C1 in confined space was determined in comparison with bulk melting. The dependence of pore radius R on the decrease of melting temperature ΔT is described by the following equation:

$$R = \frac{A}{\Delta T} + B \quad (1)$$

where A and B are the thermoporometric constants for the studied system. In this study R for examined NC+C1 samples were calculated based on method and parameters described in the previous work [12].

On the basis of melting enthalpy of low molecular component C1 in the prepared mixtures the amount of

Table 1 Parameters of the studied NC samples

| Sample denotation | Nitrogen content/% | Viscosity of 1% solutions in acetone/mPa s | $A_{BJH}/\text{cm}^2 \text{g}^{-1} \cdot 10^2$ | $V_{BJH}/\text{cm}^3 \text{g}^{-1} \cdot 10^2$ |
|-------------------|--------------------|--|--|--|
| M1 | 12.16 | 73.6 | 12.1 | 3.6 |
| M2 | 12.15 | 94.4 | 12.8 | 4.0 |
| M3 | 12.18 | 200.9 | 12.4 | 4.1 |

non-crystallizing C1 molecules equivalent to NC unit (1 ring) can be calculated from the following equation:

$$n = \frac{x_{w1} - (\Delta H_{ml}^2 / \Delta H_{ml}^0)}{M_1 / M_2 (1 - x_{w1})} \quad (2)$$

where ΔH_{ml}^0 is the melting enthalpy of bulk C1, ΔH_{ml}^2 is the melting enthalpy of C1 in NC+C1 mixtures for consecutive melting processes, x_{w1} is the mass fraction of C1, M_1 and M_2 are molar masses of C1 and NC unit (ring). The value of n determines the ability of C1 molecules to interact with NC. These C1 molecules do not undergo the phase transition and are adsorbed on the surface of NC chains.

The DSC curve registered during subsequent heating of the sample in method III is presented in Fig. 1. The shape of this curve indicates that glass transition process occurred. This can be assigned to the effect of freezing of structures formed at high temperatures during the first heating of the sample. The heat capacity change Δc_p corresponds to the amount of glass phase in the sample. The fraction of glass phase can be calculated from the equation:

$$x^a = \frac{\Delta c_p}{\Delta c_p^0} \quad (3)$$

where Δc_p^0 is the heat capacity change for pure C1.

Results and discussion

Properties of mixture M1

Nitrocellulose M1 was mixed with C1 and gave mixture with the mass fractions of NC $x_{wNC}=0.0309$. In Table 2 the following parameters are summarized: samples storing periods t_s , time between successive measurements t_p and number of melting process during DSC experiments (Lp). These parameters describe the thermal history of the specific sample.

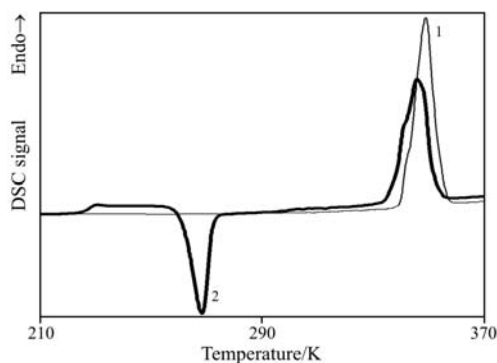


Fig. 1 Typical DSC melting and glass transition curves of C1 for M1 mixture obtained by the method III: 1 – the first heating ($Lp=2$) and 2 – ($Lp=3$) the second heating

On the DSC curves presented in Fig. 1 the thin line shows the first heating and the thick one the second process. For the first experiment only one peak resulting from the melting process is observed. There is a small inflection point visible on the low-temperature shoulder of this peak. It can be interpreted as the melting process in confined space. The parameter n achieves value of 3.5 for the measurement performed after $t_p=72.1$ h. In the next measurement performed after $t_p=0.3$ h thermal effect of glass transition occurred at 226.5 K and heat capacity change $\Delta c_p=0.485 \text{ J g}^{-1}$, what corresponds to the $x^a=0.77$. The value of the parameter $n=9.4$ calculated from the Eq. (2) is high.

It follows from the n values listed in Table 2 that during subsequent measurements carried out after short intervals t_p , the highest value of $n=9.4$ is reached. This value is also very reproducible. When the t_p are longer this parameter decreases and obtains the value of $n=2.4$. The eleventh melting process was conducted after 13246 h of sample storing. For this experiment only one melting peak is observed and value $n=2.7$ is calculated. This effect proves that the number of small pores in NC is decreasing. For the next measurement performed after 1.8 h also one melting peak is registered and value $n=2.4$ is reached. Moreover the value of n does not increase for the experiments repeated after short intervals.

In Fig. 2 selected DSC curves obtained for sample M1 using method I are shown. The results represent melting processes conducted successively after different intervals. When the measurement was repeated after the shortest time the melting process occurred in confined space (pores) of different dimensions. The pore sizes can be analysed taking into con-

Table 2 Experimental parameters for M1 mixture ($x_{wNC}=0.0309$)

| Lp | Method | t_p/h | n |
|------|--------|---------|-----|
| 2 | I | 386.4 | 3.3 |
| 3 | III | 72.1 | 3.5 |
| 4 | III | 0.3 | 9.4 |
| 5 | I* | 76 | 2.5 |
| 6 | I* | 21.8 | 2.6 |
| 7 | I** | 1.5 | – |
| 8 | I** | 68.4 | – |
| 9 | I* | 5.5 | 9.4 |
| 10 | I** | 19.8 | – |
| 11 | I | 13246 | 2.7 |
| 12 | I | 1.8 | 2.4 |

*overlapping melting peaks, **no crystallization observed; [Lp – number of melting processes, method – used DSC method, t_p – time between successive measurements, and n – parameter n]

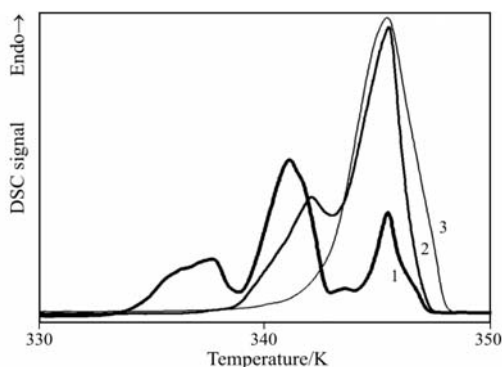


Fig. 2 DSC melting curves of C1 for M1 mixture obtained by the method I after the following time between successive measurements: 1 – $t_p=5.5$ h ($Lp=9$), 2 – $t_p=76$ h ($Lp=5$) and 3 – $t_p=13246$ h ($Lp=11$)

sideration the maximal temperatures of melting peak. It is assumed that the melting peak observed at the highest temperature responds to melting of C1 in unconfined space. For short intervals between measurements (thick line curve in Fig. 2 for $Lp=9$ and $t_p=5.5$ h) the melting process occurred in characteristic pores. It can be noticed that for the long intervals between experiments (t_p) the melting process is characterized by one peak ($Lp=11$) on DSC curve. For longer intervals t_p the migration of C1 molecules inside the porous polymeric matrix is observed. The mass transfer from smaller pores into wider ones occurs what can be explained by the formation of bigger, more stable thermodynamically crystals. The sizes of C1 crystal depend on the pore's dimensions. The walls of pores in cellulose matrix are flexible and they can change their positions. This suggest that bigger pores are created as the result of joining of sheets forming walls of smaller pores.

The pores sizes calculated on the basis of the temperature of melting peak for different values of t_p are summarized in Table 3. In the last row one can see the results of calculation for the DSC curve possessing peaks with well formed maximum that responds to the melting in unconfined space. The other results were computed taking into account estimated temperatures of peaks and they have considerable uncertainty. The relations between pores sizes $d1$, $d2$ and $d4$ can be described approximately as:

$$d2 \approx 2d1 \text{ and } d4 \approx 2d2 \quad (4)$$

Table 3 Dependence of the mean pore sizes (d) for M1 mixture upon time between successive measurements (t_p)

| Lp | $d1/\text{nm}$ | $d2/\text{nm}$ | $d3/\text{nm}$ | $d4/\text{nm}$ |
|------|----------------|----------------|----------------|----------------|
| 2 | 23.6 | 41.5 | 65.4 | 105 |
| 5 | 27.5 | – | 63.8 | – |
| 9 | 28.0 (23.7) | 50.2 | – | 114 |

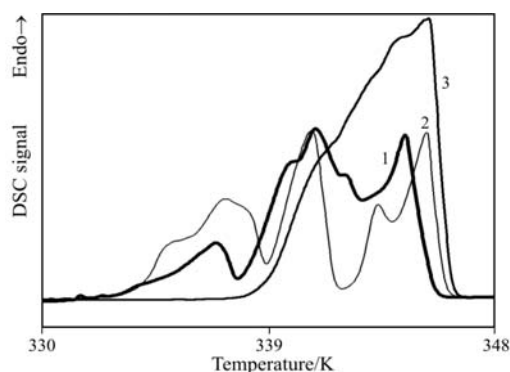


Fig. 3 DSC melting curves of C1 in confined and unconfined space for M2 mixture obtained after the following time between successive measurements: 1 – $t_p=1.6$ h ($Lp=10$), 2 – $t_p=1.7$ h ($Lp=6$) and 3 – $t_p=93.9$ h ($Lp=5$)

Properties of mixture M2

Nitrocellulose M2 was mixed with C1 and gave mixture with mass fractions of NC $x_{wNC}=0.0305$. In Fig. 3 the DSC curves of melting process of C1 in confined and unconfined space for different intervals between measurements (t_p) are presented. The shape of the DSC curves proves that there is a significant influence of t_p values on the melting process. The values of the parameter n for the subsequent measurements carried out after different intervals t_p are listed in Table 4. For the studied mixture M2 value of n ranged from 2.8 to 9.9. The phase changes are reversible even for the longest samples storing time. The results of the calculation pore size are shown in Table 5. The pore sizes and their relationships are similar as for the mixture M1.

Properties of mixture M3

In Fig. 4 selected DSC curves registered for mixture M3 after different intervals (t_p) are presented. The second

Table 4 Experimental parameters for M2 mixture ($x_{wNC}=0.0305$)

| Lp | Method | t_p/h | n |
|------|--------|----------------|-----|
| 2 | I | 385.8 | 3.6 |
| 3 | III | 71.9 | 3.7 |
| 4 | III | 0.3 | 8.9 |
| 5 | I | 93.9 | 2.8 |
| 6 | I* | 1.7 | 9.3 |
| 7 | I* | 73.1 | 2.9 |
| 8 | I* | 1.6 | 9.9 |
| 9 | I | 13269 | 2.8 |
| 10 | I* | 1.6 | 8.2 |

*overlapping melting peaks; (Lp – number of melting processes, method – used DSC method, t_p – time between successive measurements, and n – parameter n)

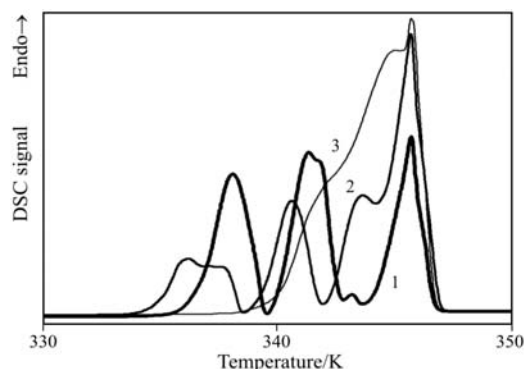


Fig. 4 Selected DSC melting curves of C1 for M3 mixture obtained after the following time between successive measurements: 1 – $t_p=1.6$ h ($Lp=13$), 2 – $t_p=1.6$ h ($Lp=9$) and 3 – $t_p=164.6$ h ($Lp=5$)

Table 5 Dependence of the mean pore sizes (d) for M2 mixture upon time between successive measurements (t_p)

| Lp | $d1/nm$ | $d2/nm$ | $d3/nm$ | $d4/nm$ |
|------|---------|---------|---------|---------|
| 6 | 27.3 | 47.7 | – | 113.9 |
| 8 | 26.4 | 48.7 | – | 98.5 |
| 10 | 28.7 | 47.7 | 60.5 | 94.7 |

melting process ($Lp=2$) for sample containing mass fractions of NC $x_{mi}=0.0305$ were carried out after 383 h using method I. The shape of the DSC curve indicates a very small effect of melting C1 in pores of radii 31.5 nm and the second one in 58.7 nm pores. The average number of C1 molecules attached to one NC mer is $n=2.6$. The melting peaks are overlapped what made calculation of the pore sizes, where the process occurred, impossible. The melting process $Lp=3$ and 4 was performed using method III. It follows from the shape of DSC curves that for $Lp=3$ only melting was possible. But for curve $Lp=4$ the glass transition at temperature $T_{gC1}=226.4$ K and heat capacity change $\Delta C_p^0=0.51$ J g⁻¹ K⁻¹ can be seen. This corresponds to the fraction of glass phase $x^a=0.81$. The influence of the intervals between experiments on parameter n are summarized in Table 6. The n values vary from 2 to 9.1. The increasing storage time of the samples can bring about changes in their pore characteristic. The smallest pores grow wider and increase their size to the values typical for medium and big pores. At the same time shift of the melting peak for the process occurring in confined space towards higher temperatures is observed. They overlap on the peaks connected with the melting process in unconfined space. The shape of peaks corresponding to the melting in the smallest pores changes during subsequent processes. This proves that the process is occurring in pores of two different privileged sizes and two partially overlapped melting peaks are observed. Also the heights of these peaks are changing what proves that the course of melting in different pores is diversified. For melting

Table 6 Experimental parameters for M3 mixture ($x_{wNC}=0.0305$)

| Lp | Method | t_p/h | n |
|------|--------|---------|------|
| 2 | I | 383.7 | 2.65 |
| 3 | III | 71.3 | 3.0 |
| 4 | III | 0.3 | 8.2 |
| 5 | I | 164.6 | 2.2 |
| 6 | I* | 1.6 | 7.4 |
| 7 | I* | 23.7 | 7.0 |
| 8 | I* | 13272.6 | 3.6 |
| 9 | I* | 1.6 | 7.8 |
| 10 | II | 8377 | 2 |
| 11 | II | 48.48 | 5.2 |
| 12 | I** | 117.9 | – |
| 13 | II* | 1.6 | 9.1 |

*overlapping melting peaks,

**no crystallization observed; (Lp – number of melting processes, method – used DSC method, t_p – time between successive measurements, and n – parameter n)

Table 7 Dependence of the mean pore sizes (d) for M3 mixture upon time between successive measurements (t_p)

| Lp | $d1/nm$ | $d2/nm$ | $d3/nm$ | $d4/nm$ |
|------|---------|---------|---------|---------|
| 2 | – | – | 58.7 | – |
| 5 | – | – | 59.2 | – |
| 6 | 28.8 | 43.52 | – | 130 |
| 7 | 28.3 | 43.6 | – | 121 |
| 8 | 23.2 | 38.5 | – | – |
| 9 | 23 | 42.7 | – | 104 |
| 13 | 28.5 | 49.5 | – | 88 |

process $Lp=13$ on DSC curve only one single peak is observed which can be assigned to the bigger pores. The pore sizes ($d1$) calculated at the maximum of melting peaks are varying from 22.7 to 23.7 and from 28.5 to 28.8 nm. The influence of samples storing time on pore sizes is summarized in Table 7. During the initial stage of experiments e.g. for the long samples storing the melting process of C1 is observed in confined space, limited to pores of sizes up to 59 nm. This value can be expressed as triple size of $d1$. The forming of these pores cannot be observed for the subsequent measurements for the same sample.

Conclusions

The studies carried out on the mixtures prepared from three different NC obtained from linters and C1 showed that DSC curves of melting process in con-

finned and unconfined space for short intervals between measurements were different. It was also found that the influence of increasing time between subsequent processes was substantial. The main assumption for estimating of pore sizes was that their walls are formed from planes created from ordered NC microfibrils. Our results based on melting process provided evidence for the presence of four different kinds of pores of increasing sizes e.g. d_1 , d_2 , d_3 and d_4 . The size of pores d_1 varied from 19 to 29 and d_2 from 38 to 50 nm. The pores d_3 were found for longer periods of samples storing and were about 64 nm. The size of pores d_4 were estimated from 90 to 130 nm and their role in melting of C1 was insignificant. For broad pores the DSC melting peak overlapped with peak of melting process in unconfined space. From this reason the calculations of their contribution in the total porosity of NC were rather approximate. The observed changes during long storage time of NC+C1 mixtures were connected with the migration of C1 from small pores to bigger ones.

Based on the total melting enthalpy of the defined mixtures the values of parameter n were established. For short time t_p (about 1.7 h) it was close to $n=9$. But this was unstable state and the C1 molecules due to their thermal movements relocated and could crystallised or recrystallised. For long time t_p these values varied from 2 to 3.5 for different NC samples.

References

- 1 D. Klemm, B. Philipp, T. Heinze, U. Heinze and W. Wagenknecht., *Comprehensive Cellulose Chemistry*, tom 1. Wiley-VCH, 1998, pp. 22–25.
- 2 D. F. Miles, *Cellulose Nitrate, The Physical Chemistry of Nitrocellulose, its Formation and Use*, Imp. Chem. Ind. Ltd., Oliver and Boyd. 1955, pp. 10–11.
- 3 K. Wickholm, P. T. Larsson and T. Iversen, *Carbohydr. Res.*, 312 (1998) 123.
- 4 A. Książczak, A. Radomski and T. Zilenkiewicz, *J. Therm. Anal. Cal.*, 74 (2003) 559.
- 5 Yu. M. Mikhailov, N. V. Chukanov and V. S. Smirnov, *Izv. Akad. Nauk. Ser. Khim.*, 3 (1999) 487.
- 6 B. W. Brodman, M. P. Devine and M. T. Gurbarg, *J. Appl. Polym. Sci.*, 18 (1974) 943.
- 7 M. Brun, A. Lallemand, J.-F. Quinson and Ch. Eyraud, *Thermochim. Acta*, 21 (1977) 59.
- 8 L. G. Homshaw, *J. Thermal. Anal.*, 19 (1980) 215.
- 9 J. F. Quinson, N. Tchikam, J. Dumas, C. Bovier and J. Serughetti, *J. Non-Cryst. Solids*, 99 (1988) 151.
- 10 A. Książczak and T. Książczak, *J. Thermal. Anal.*, 54 (1998) 323.
- 11 A. Książczak, T. Książczak and M. Ostrowski, *J. Therm. Anal. Cal.*, 74 (2003) 575.
- 12 A. Książczak and M. Ostrowski, *J. Therm. Anal. Cal.*, 77 (2004) 341.
- 13 A. Książczak and T. Wolszakiewicz, *J. Therm. Anal. Cal.*, 67 (2002) 751.
- 14 A. Książczak and T. Wolszakiewicz, *J. Therm. Anal. Cal.*, 77 (2004) 353.
- 15 G. Herder and W. P. C. de Klerk, *J. Therm. Anal. Cal.*, 85 (2006) 169.
- 16 L. Jizhen, F. Xuezhong, F. Xiping, Z. Fengqi and H. Rongzu, *J. Therm. Anal. Cal.*, 85 (2006) 779.

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