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## Non-isothermal kinetics of $\epsilon$ -caprolactam blocked polyisocyanate thermal dissociation

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*The differential scanning calorimetry method was used to investigate the kinetics of thermal dissociation of  $\epsilon$ -caprolactame blocked polyisocyanate under non-isothermal conditions using isoconversion approach. The values of kinetic parameters of the process calculated using several theoretical models (Kissinger, Ozawa–Flynn–Wall, Friedman) are in good agreement. Differential scanning calorimetry with temperature modulation denotes the structural changes in the system under heating and consumption of considerable part of NCO-groups at the same time with thermal dissociation.*

**Keywords:** blocked isocyanate, differential scanning calorimetry, non-isothermal kinetics, activation energy, reaction order.

### Introduction.

Isocyanates are heterocumulenes that can generate a wide spectrum of reactions particularly with alcohol or amine as well as self-additions. Owing to high reactivity and toxicity of isocyanate molecules synthesis using these reagents and their storage require special precautions. Application of isocyanates in latent form, e.g. blocked isocyanates, essentially simplifies carrying out of the reaction and therewith is very important in view of technical and economic aspects. Blocked isocyanates are latent reagents that can release high reactive NCO-groups under heating. They are used in broad range of almost every type of coatings as well as in various non-coatings applications [1–3].

Reaction, where one of the reagents is blocked isocyanate, passes through at least two parallel processes. First of them is release of free isocyanate groups and second is consumption of NCO-groups in main reaction. Information on the factors influencing the path of competing reactions in polymer compositions modified by blocked isocyanates are of interest for further development of methods to modify polymer materials.

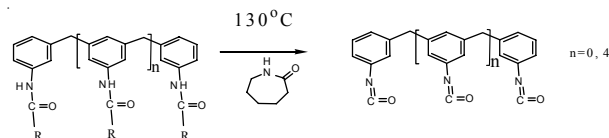
Kinetics of NCO-groups formation in the process of blocked isocyanate thermal dissociation can have essential influence on the isocyanate reactivity as well as on main reaction rate and mechanism. In present paper the DSC method was used to investigate the kinetic of thermal dissociation of  $\epsilon$ -caprolactame blocked polyisocyanate (PICb) under non-isothermal conditions using isoconversion approach.

### Materials and methods.

Methylene diphenyl type polyisocyanate is a product of aniline phosgenation. It is homologue mixture and consists of 40 to 70 % of dimeric compound, 20 to 60 % of

tetramer, 1 to 5 % trimer and hexamer.

PICb obtained according to [4] is multifunctional latent reagent with melting range of 75 to 95 °C, NCO-group deblocking temperature from 125 to 130 °C. Thermal dissociation of PICb release reactive NCO-groups according to scheme



The kinetics of thermal dissociation of  $\epsilon$ -caprolactame blocked polyisocyanate was investigated via DSC method. DSC curves were obtained using TA Instruments DSC Q2000 at heating rates of 5, 10, and 20 degree/min. The conversion degree was calculated using DSC data in proportion to the change per time unit of area under heat

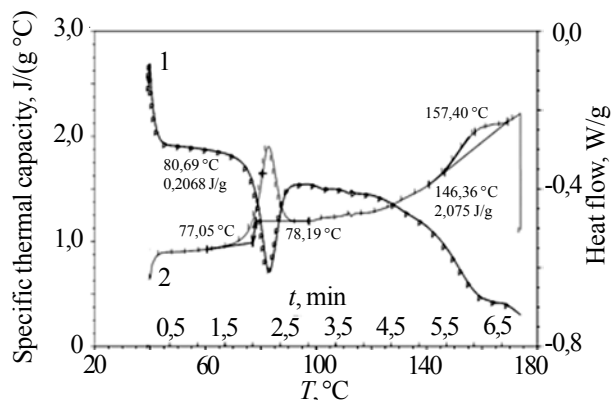


Fig. 1. Temperature dependence of specific thermal capacity (1) and heat flow (2) for PICb thermal dissociation at heating rate of 20 degree /min.

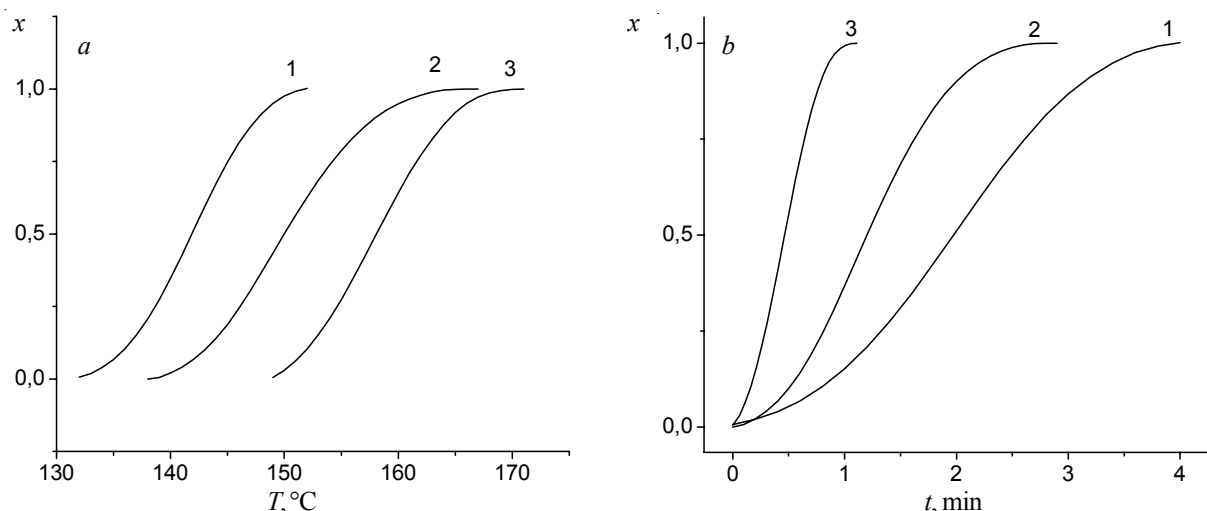


Fig. 2. Temperature (a) and time (b) dependences of conversion degree of PICb under heating: 1 –  $\beta = 5$  degree/min; 2 –  $\beta = 10$  degree/min; 3 –  $\beta = 20$  degree/min.

flow curve in temperature region 130 – 170 °C that corresponds to PICb thermal dissociation.

Activation energy was calculated according to model-free isoconversion methods: Kissinger, Ozawa–Flynn–Wall, Friedman [5–8].

**Results and discussion.**

The typical temperature dependence of specific thermal capacity and heat flow for PICb thermal dissociation illustrates Fig. 1. Fig. 2 shows plots of conversion degree (x) versus temperature (T) and time (t).

Obtained kinetic curves are S-shaped owing to the increase of reaction rate with increasing of temperature. As it can be seen, the temperature of the reaction beginning depends on sample heating rate ( $\beta$ ). It increases with growing of the heating rate, whereas the temperature range (interval) of the reaction remains almost unchanged (Fig. 2a). Increase of heating rate value reduces time to reach the same conversion degree (Fig. 2b).

Using commonly applied assumption that the conversion degree during a reaction is the product of two functions, one depending on the fraction converted, and the other depending on the temperature according to Arrhenius type dependency, reaction rate can be described by the kinetic equation 1.

$$dx/dt = f(x)k_0 \exp(-E_{act}/RT), \tag{1}$$

where  $dx/dt$  – is conversion rate,  $f(x)$  – function determining the conversion rate dependence on conversion degree  $x$ ,  $k_0$  and  $E_{act}$  – temperature independent reaction parameters – frequency factor and activation energy,  $R$  – absolute gas constant,  $T$  – temperature.

For non-isothermal experiments, the reaction rate at all times depends on both  $f(x)$  and  $k(T)$ , and the determination of  $f(x)$ ,  $k_0$  and  $E_{act}$  (kinetic triplet) is an interlinked problem.

According to given on Fig. 2b dependencies the maximum reaction rates are 1,51 c<sup>-1</sup>, 0,67 c<sup>-1</sup> and 0,42 c<sup>-1</sup> at heating rates  $\beta$  of 20 degree/min, 10 degree/min and 5 degree/min, correspondingly.

To determine the kinetic triplet isoconversion methods involve evaluation of the temperatures corresponding to fixed values of  $x$  from the experiments at different heating rates  $b$ . Typically, three or more experiments are required with different heating rates.

Kissinger method approximates a fixed stage of conversion as the stage of reaction at which the maximum rate of conversion is achieved. For a given DSC curve with the heating rate  $b$  the maximum conversion rate is observed at the peak temperature,  $T_p$  [5, 6].

$$\ln(\beta/T_p^2) = \ln k_0 R/E_{act} - E_{act}/RT_p. \tag{2}$$

Obtained Kissinger plot of  $\ln(\beta/T_p^2)$  against  $1/T_p$  for PICb thermal dissociation with heating rates of 5, 10 and 20 degree/min can be approximated using linear equation  $y = 24,74 - 14693,2x$  with correlation coefficient  $R = 0,997$ .

Linearity of the relationship of  $\ln(\beta/T_p^2)$  and  $1/T_p$  indicates the first order kinetics of PICb dissociation process. The result agrees with proposed scheme of PICb thermal dissociation. Activation energy calculated according Kissinger method with reference points  $T_p$  on temperature dependence of the conversion degree is 121,3 kJ/mol. Pre-exponential factor value was calculated according to  $\text{tg}(\phi) = E_{act}/R$  and  $y(0) = \ln(k_0 R/E_{act})$ .  $\ln k_0 = 14$ .

The isoconversional method of Ozawa–Flynn–Wall (OFW) [5, 7] assumes that the conversion function  $f(x)$  does not change with the variation of the heating rate for all values of the degree of conversion. Eq. (1) in OFW formalism is rewritten in an integral form as

$$\ln(\beta) = \ln(k_0 E_{act}/R) - \ln f(x) - E_{act}/RT. \tag{3}$$

Obtained OFW plot of  $\ln(\beta)$  against  $1/T$  for PICb thermal dissociation with heating rates of 5, 10 and 20 degree/min can be approximated using linear equation  $y = 33,84 + 15439,3x$  with correlation coefficient  $R = 0,993$ .

Activation energy calculated according OFW method with reference points  $T_p$  on temperature dependence of the conversion degree is 128,3 kJ/mol. Pre-exponential factor value was calculated according to  $\text{tg}(\phi) = E_{act}/R$  and  $y(0) = \ln(k_0 E_{act}/R)$ .  $\ln k_0 = 29$ .

Table. The values of kinetic parameters of the PICb thermal dissociation calculated using several isoconversion models

Kinetic parameters	Isoconversion models		
	Kissinger [6]	OFW [7]	Friedman [8]
$E_{act}$ , kJ/mol	121,3	128,3	126,4
$\ln k_0$	14	29	28

Under the isoconversion assumption of Friedman method [5, 8] in linear heating experiment at various heating rates the function  $f(x)$  at fixed stage of conversion will be a constant. Therefore, the plot of  $\ln(dx/dt)$  against  $1/T$  results in a straight line with the slope being  $-E_{act}/R$ .

Eq. (1) in Friedman method formalism is rewritten as

$$\ln(dx/dt) = (E_{act}/RT) - \ln(f(x)). \quad (4)$$

Obtained Friedman plot of  $\ln(dx/dt)$  against  $1/T_p$  for PICb thermal dissociation with heating rates of 5, 10 and 20 degree/min can be approximated using linear equation  $y = 37,48 - 15179,1x$  with correlation coefficient  $R=0,998$ .

Activation energy calculated according Friedman method with reference points  $T_p$  on temperature dependence of the conversion degree is 126,4 kJ/mol. Pre-exponential factor value was calculated according to  $\lg(\varphi) = E_{act}/R$  and  $y(0) = \ln(k_0 E_{act}/R)$ .  $\ln k_0 = 28$ .

The values of activation energy of the process calculated using several isoconversion models correlate well (Table).

Isoconversion methods allow not only determine the kinetic parameters ( $E_{act}$  and  $k_0$ ) of the process but also identify some special reaction aspects.

As it can be seen (Fig. 3) in the area where conversion degree is more than 0,7 the inclination of lines changes. The fact can denote that thermal dissociation of PICb proceeds in two stages or that simultaneously competing reaction occurs. Taking into account the possibility of homo-addition of NCO-groups under experiment conditions [9] the second supposition is more reliable.

Results of differential scanning calorimetry with application of temperature modulation (TMDSC) confirm

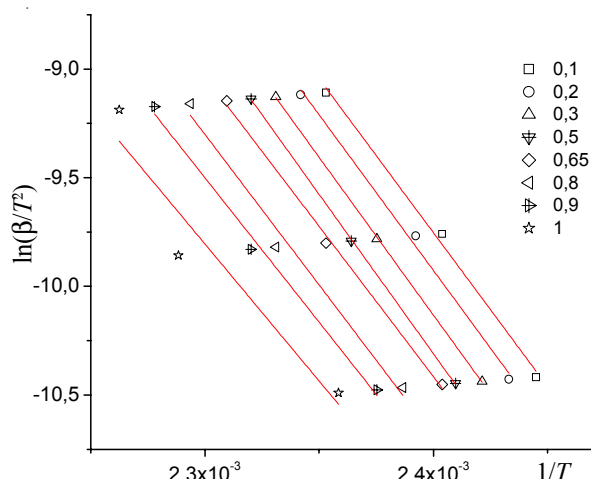


Fig. 3. The Kissinger type dependences obtained from the DSC curves at various conversion degree

the last assertion.

The differential scanning calorimetry with application of temperature modulation involves the deconvolution of the heat-flow rate into one part that follows modulation (the reversing part), and one, that does not (the nonreversing part) [10]. The term reversing is used to distinguish the raw TMDSC data from data proven to be thermodynamically reversible. The TMDSC thermograms of PICb thermal dissociation illustrates Fig. 4.

The DCS curves at Fig. 4a (first run) are characteristic by presence of melting peak at 75 °C in total  $C_p$  and in its nonreversing part where as the reversing  $C_p$  curve is typical to amorphous system. Such peak is absent in second run TMDSC curves where as reversing  $C_p$  curve remains be typical to amorphous system. Within temperature interval of 130 °C to 150 °C characteristic to PICb deblocking process three times reduction of thermal effect is observed - from 1,57 J/g during first run to 0,5 J/g during second run. The facts show consumption of considerable part of NCO-groups at the same time with thermal dissociation.

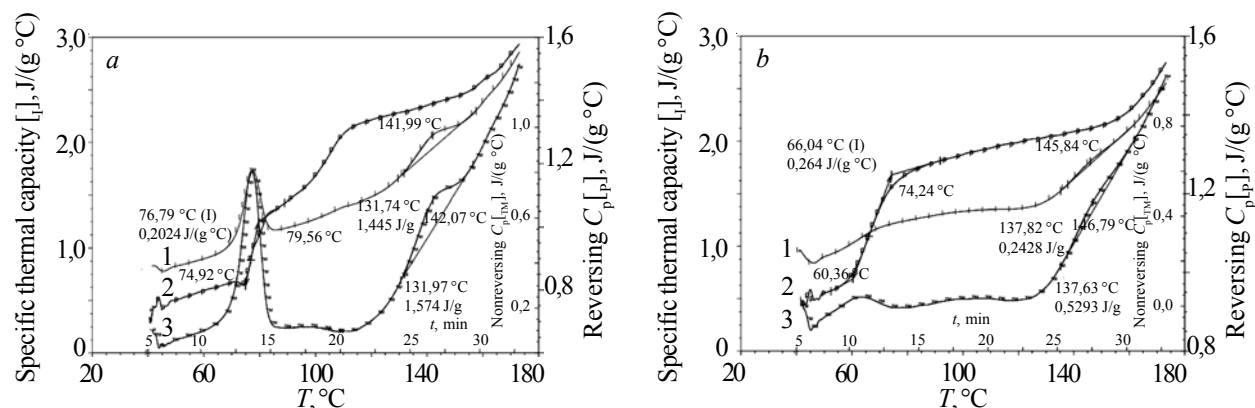


Fig. 4. Temperature dependence of specific thermal capacity: total (1); reversing part (2) and nonreversing part (3) for PICb thermal dissociation at heating rate 5 degree /min. a – first run, b – second run

### Conclusion.

Analysis of non-isothermal kinetics of  $\epsilon$ -caprolactam blocked polyisocyanate thermal dissociation using model-free isoconversion methods indicates the first order of the reaction that agrees with proposed scheme of PICb thermal dissociation. The values of kinetic parameters of the process calculated using several isoconversion models correlate well.

Change of the inclination of isoconversion lines obtained from the DSC curves at various conversion

degrees and possibility of homo-addition of released NCO-groups under experiment conditions allows conclude that during thermal dissociation of PICb competing reaction occurs.

Differential scanning calorimetry with temperature modulation denotes the structural changes in the system under heating from semi crystalline to amorphous as well as consumption of considerable part of NCO-groups at the same time with thermal dissociation.

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## Неізотермічна кінетика термічної дисаціації поліізоціанату, блокованого $\epsilon$ -капролактамом

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*Кінетичні дослідження термічної дисоціації поліізоціанату, блокованого  $\epsilon$ -капролактамом в неізотермічних умовах досліджено методом диференційної скануючої калориметрії різними підходами. Значення кінетичних параметрів процесу розраховано за допомогою кількох теоретичних моделей (Кісенджер, Озава-Флін-Вол, Фрідман). За даними диференціальної скануючої калориметрії з температурою модуляцією вказує на структурні зміни в системі при нагріванні і споживання значної частини NCO-груп одночасно з термічною дисоціацією.*

**Ключові слова:** блокований ізоціанат, диференційна скануюча калориметрія, неізотермічна кінетика, енергія активації, порядок реакції.

## Неізотермическая кинетика термической диссоциации полиизоцианата, блокированного $\epsilon$ -капролактамом

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*Кинетические исследования термической диссоциации полиизоцианата, блокированного  $\epsilon$ -капролактамом в неізотермических условиях исследовано методом дифференциальной сканирующей калориметрии различными подходами. Значение кинетических параметров процесса рассчитано с помощью нескольких теоретических моделей (Кисенджер, Озава-Флин-Волынский, Фридман). По данным дифференциальной сканирующей калориметрии с температурой модуляцией указывает на структурные изменения в системе при нагревании и потребления большого числа NCO-групп одновременно с термической диссоциацией.*

**Ключевые слова:** блокированный изоцианат, дифференциальная сканирующая калориметрия, неізотермических кинетика, энергия активации, порядок реакции.