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Kinetics of melamine phosphate thermal decomposition in DSC studies

Mariusz Nowak[1] · Barbara Cichy[1] · Ewa Kużdżał[1]

Abstract This paper presents the results of study of the kinetics of two-stage condensation of melamine orthophosphate to melamine pyrophosphate and subsequently to melamine polyphosphate. The investigations were conducted under non-isothermal conditions and at constant rate of sample heating. Five different heating rates were applied: 40, 20, 10, 5, 2 K min^{-1}. The activation energy of the process was determined using the approximate Kissinger method and the isoconversional Kissinger–Akahira–Sunose method. The thus determined activation energy is largely dependent on the extent of conversion, indicating the complexity of analyzed process. A complete analysis of the process was presented. Presented calculation of the full kinetic models was best described by stage I equation F1 Mampel and stage II Avrami–Erofeev equation A2. These equations have the best statistical fit. Theoretical kinetic curves were compared with the experimental data, achieving high compliance of theoretical curves with the experimental data.

Keywords Flame retardants · Melamine phosphate · Reaction kinetics · Thermal analysis

List of symbols

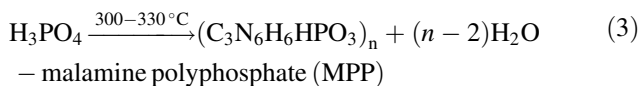|	
A	Pre-exponential factor in Arrhenius equation
E	Activation energy
$f(\alpha)$, $h(\alpha)$	Kinetic component of the reaction rate equation
$g(\alpha)$	Integrated form of the reaction model
k	Reaction rate constant
m, n	Coefficients in the kinetic equation
R	Gas constant
T	Temperature
T_p	Temperature of the peak maximum
v, $d\alpha/dt$	Reaction rate
α	Extent of conversion
β	Heating rate
γ	Significance level
t_γ	Student's t test value
N	Number of measurements

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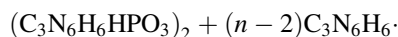
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Introduction

Melamine phosphates of various degree of polycondensation such as melamine phosphates (MP), melamine polyphosphates (MPP) and melamine pyrophosphates (MDP) are used increasingly as flame retardants (FR), particularly as additives to plastics [1–6]. Products made of plastics consist flame retardants. Until this moment, the flame retardants were halogenated compounds which decompose in increased temperature releasing additional harmful substances. According to REACH classification, many of chlorine derivative flame retardants are classified as PBT substances (persistent, bioaccumulative and toxic). Due to this fact, their application is prohibited or amount is strictly limited. Regarding to the above, it is very important to develop technologies to produce halogen-free flame retardants. In one of the groups of these products are materials based on melamine phosphate in various degrees of polycondensation. These agents, as compared to traditional flame retardants, are more environment friendly, as at elevated temperatures they do not release halogenated

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compounds, in particular toxic compounds of bromine. Melamine phosphates contain less phosphorus than the popular ammonium polyphosphate. However, the decomposition of the melamine ring at temperatures above 300 °C occurs with the absorption of heat from the surroundings due to release of the nitrogen. This makes melamine phosphates useful as flame retardants for polymeric materials that require high-temperature processing or that are designed for use at elevated temperatures.

MP is widely used to improve fire resistance of many polymeric materials and coatings [1, 3–6] and is an important intermediate for obtaining melamine polyphosphate (MPP) [7, 8]. Melamine polyphosphate (MPP) exhibits excellent thermal resistance and no significant mass loss up to temperatures of over 300 °C [1, 7, 9, 10]. The effects of MPP application in various polymeric materials, such as polyamides [11], polypropylene [7, 12], epoxy compositions [13] and polyurethane [14], have been described in many publications. Melamine phosphates have to be stable in the molding process of plastics. However, they have to decompose during the fire and limit the spread of flame. Describing its thermal properties limits their range of applications. Temperature of retardant decomposition has to be strictly connected with temperature of polymer degradation. This is a reason why phosphates at different condensation degree are applied.

There are many methods of preparing melamine polyphosphate described in the literature; two of them were described back in the 1940s [15]. One consisted in producing melamine orthophosphate suspension from orthophosphoric acid and melamine followed by calcination at 250–270 °C. The other consisted in reacting melamine with tetrasodium pyrophosphate in a solution with an addition of hydrochloric or nitric acid. Modern methods involve reacting melamine with phosphoric or polyphosphoric acid at ambient temperature. Preparing MPP as flame retardant component in plastics was described in many patents [16–20]. Solid particles of sparingly water soluble melamine suspended in water react quite rapidly with phosphoric acid to form a solid precipitate. The reaction product requires post-curing at 250–350 °C. The reaction may be carried out either in batch [3, 7, 8, 21] or continuous mode [22].

The synthesis of melamine phosphate, pyrophosphate and polyphosphate can be described by the following equations:

$$C_3N_6H_6 + H_3PO_4 \rightarrow C_3N_6H_6 \cdot H_3PO_4$$
$$- \text{melamine phosphate (MP)} \quad (1)$$

$$2C_3N_6H_6 \cdot H_3PO_4 \xrightarrow{250-300\,°C} (C_3N_6H_6HPO_3)_2 + H_2O$$
$$- \text{melamine pyrophosphate (MDP)}$$
$$(2)$$

$$(C_3N_6H_6HPO_3)_2 + (n-2)C_3N_6H_6 \cdot$$
$$H_3PO_4 \xrightarrow{300-330\,°C} (C_3N_6H_6HPO_3)_n + (n-2)H_2O \quad (3)$$
$$- \text{malamine polyphosphate (MPP)}$$
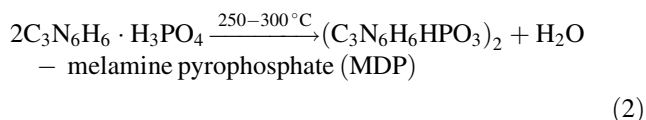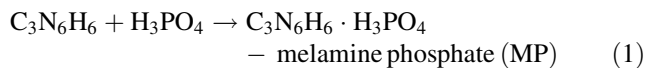
The processes, however, particularly those that proceed in solid state, are in fact more complex. Upon heating, melamine phosphate undergoes condensation followed by thermal decomposition [1, 9, 10]. The theoretical mass loss in the first stage of condensation (Eq. 2) due to the water release equals 4.0 %. This has been confirmed experimentally [7, 10]. The second stage of condensation (Eq. 3) is less straightforward; apart from simple condensation of the pyro form to poly forms which proceeds with release of water, also thermal decomposition occurs simultaneously; moreover, products of various degree of condensation are obtained. To establish exact composition of product, both thermal analysis (TG/DTG, DSC) and spectroscopy (FTIR, 31P and 13C NMR in solid state, XRD) can be applied [1, 9, 10, 17, 23, 24].

The aim of the work was to study the kinetics of melamine phosphate decomposition (dehydration) to pyrophosphate and then to polyphosphate. Earlier investigations of thermal decomposition of melamine phosphate focused mainly on melamine pyrophosphate preparation and involved TG/DTG techniques [8, 22, 25]. In previous work, we determined kinetic parameters of the first stage of condensation (formation of melamine pyrophosphate) with the use of TG/DTG method [26]. In this work, to determine kinetic relations of two subsequent stages of melamine polyphosphate synthesis, we applied differential scanning calorimetry (DSC). We used the Kissinger method, Kissinger–Akahira–Sunose isoconversional method and reaction model fitting method to obtain kinetic parameters and establish a kinetic model of two last stages of melamine polyphosphate synthesis, as a part of work on developing of a method of production of melamine phosphate flame retardant.

Kinetics of heterogeneous reactions

In a general case, the rate of a heterogeneous reaction may be expressed by Eq. (4) [27–30]:

$$v = \frac{d\alpha(t)}{dt} = F[\alpha(t), T] \quad (4)$$

If one assumes that the terms that are temperature-dependent and conversion-dependent are mutually independent and separable, then the Eq. (4) can be reformulated as follows:

$$v = \frac{d\alpha}{dt} = F(\alpha, T) = k(T) \cdot f(\alpha) \quad (5)$$

The $k(T)$ component is a temperature-dependent function, and $f(\alpha)$ describes the kinetic model of the reaction. If these assumptions are adopted, the value of $f(\alpha)$ is a function of a conversion degree and depends on the reaction mechanism, but not on the temperature. In many cases, the temperature component is described, to a good approximation, by the Arrhenius Eq. (6):

$$k(T) = A\exp\left(-\frac{E}{RT}\right) \tag{6}$$

where A—constant dependent on reaction mechanism (the so-called pre-exponential factor), E—activation energy, R—gas constant.

Substituting the relationship (6) into Eq. (5) gives the basic form of kinetic Eq. (7):

$$v(t) = \frac{\mathrm{d}\alpha(t)}{\mathrm{d}t} = A\mathrm{e}^{-\frac{E}{RT(t)}} \cdot f[\alpha(t)] \tag{7}$$

The differential Eq. (5) may be written in an integral form, and then, for the known and integrable forms of function $f(\alpha)$, it takes the form (8):

$$g(\alpha) = \int \frac{\mathrm{d}\alpha}{f(\alpha)} = \int k(T) \cdot \mathrm{d}t \tag{8}$$

For complete kinetic analysis, the goal is to determine three kinetic quantities: activation energy (E), pre-exponential factor (A) in the Arrhenius equation, and kinetic equation $f(\alpha)$ and $g(\alpha)$ that best describes the process. In the numerical sense, the task is to find proper values of E, A and parameters a, b, n in function $f(\alpha)$, so that the relationship (9) is satisfied:

$$\sum_{i=1}^{N} \left\{ v(t_i) - A\exp\left(-\frac{E}{RT(t_i)}\right) \cdot f[a, b, n, \alpha(t_i)] \right\}^2 \rightarrow \min \tag{9}$$

In the case of complex multistage processes, when function $f(\alpha)$ includes some additional parameters, despite Eq. (9) being numerically consistent, the determined values of E, A may be subject to considerable error or even deprived of any physical sense. In view of the difficulties in carrying out a full kinetic analysis and of often improper interpretation of the results obtained, a number of simplified methods have been developed for use in thermal analysis.

A simple and approximate method of determination of activation energy that is often applied is the Kissinger method [31] and modifications thereof. It is based on the dependence of temperature T_m of the extreme DTG or DSC signal on the sample heating rate β.

Differentiation of Eq. (7) and equating it to zero at the temperature of maximum signal intensity leads to the following relationship (10):

$$\frac{\mathrm{d}^2\alpha}{\mathrm{d}t^2} = \left[\frac{E\beta}{RT_p^2} + Af'(\alpha_p)\exp\left(\frac{-E}{RT_p}\right) \right] \left(\frac{\mathrm{d}\alpha}{\mathrm{d}t}\right) = 0 \tag{10}$$

where $f'(\alpha) = \mathrm{d}f(\alpha)/\mathrm{d}\alpha$, and the p index denotes values at the temperature of the peak, that is at the point of maximum signal level. Rearrangements of the equation lead to the basic form of the Kissinger Eq. (11):

$$\ln\left(\frac{\beta}{T_p^2}\right) = \frac{-E}{RT_p} + \mathrm{const} \tag{11}$$

In Kissinger method, activation energy is determined by plotting the dependence of $\ln\left(\beta \cdot T_p^{-2}\right)$ versus T_p^{-1}. The slope of the straight line obtained is equal to $-E/R$, which enables the calculation of the activation energy of the reaction under study. This method provides an approximate, averaged value of activation energy.

More precise methods of determining the values of kinetic parameters are the so-called isoconversional methods [27, 32]. These methods assume that the activation energy of a process is independent of temperature, and the reaction rate at given degree of conversion α is a function of temperature only. Under these assumptions, the integral relationship can be expressed in the form of Friedman's formula (12):

$$\ln\left(\frac{\mathrm{d}\alpha}{\mathrm{d}t}\right)_{\alpha,i} = \ln[f(\alpha)A_\alpha] - \frac{-E_\alpha}{RT_{\alpha,i}} \tag{12}$$

where for each degree of conversion α, the value of E_α is determined from the slope of the plot of $\ln(\mathrm{d}\alpha/\mathrm{d}t)_{\alpha,i}$ versus $1/T_{\alpha,i}$. The i index denotes various temperature programs, whereas $T_{\alpha,i}$ is the temperature at which the degree of conversion α is reached in the i-th temperature program.

The principal problem in determining kinetic parameters by means of isoconversional methods is finding the accurate solution of the $Y(T)$ integer of Eq. (13):

$$g(\alpha) = \int_0^\alpha \frac{\mathrm{d}\alpha}{f(\alpha)} = \frac{1}{\beta} \int_{T_0}^T A\exp\left[-\frac{E}{RT}\right]\mathrm{d}T = Y(T) \tag{13}$$

Approximate solution gives the general form (14):

$$\ln\left(\frac{\beta_i}{T_{\alpha,i}^B}\right) = \mathrm{const} - C\frac{E_\alpha}{RT_\alpha} \tag{14}$$

where B and C are parameters determined by the approximate solution of the kinetic equation.

There are various known and applied forms of the approximate solution of Eq. (13). Depending on the approximate values of B and C used, Eq. (14) can take the form of, for instance, Ozawa and/or Flynn and Wall Eq. (15), Kissinger–Akahira–Sunose Eq. (16) or Starink Eq. (17):

$$\ln(\beta_i) = \text{const} - 1{,}052 \frac{E_\alpha}{RT_\alpha} \tag{15}$$

$$\ln\left(\frac{\beta_i}{T_{\alpha,i}^2}\right) = \text{const} - \frac{E_\alpha}{RT_\alpha} \tag{16}$$

$$\ln\left(\frac{\beta_i}{T_{\alpha,i}^{1,92}}\right) = \text{const} - 1{,}0008 \frac{E_\alpha}{RT_\alpha} \tag{17}$$

Another method was proposed by Lyon and presented in [33]. The isoconversional method may be presented as a "finite difference (FD) formula", similar to the Kissinger equation or as an "analytic derivative (AD) formula", similar to the Ozawa equation. Both formulas, FD and AD, enable obtaining identical values in direct calculations without the need to apply iterative methods. The frequency factor can be calculated from the FD formula when one of the reaction models is adopted. Assuming that $E \gg RT$ and $T_0 \ll T$, the approximate value of the integral in Eq. (18) is:

$$Y(T) = \frac{ART^2 \exp\left[\frac{E}{RT}\right]}{\beta(E + 2RT)} \tag{18}$$

As suggested in [7], the relationship (18) is more accurate than other formulas of this type presented in the literature, and it was a basis from which two equations were derived for use in direct calculations of kinetic parameters. One of these equations, upon logarithmic and appropriate rearrangements, takes the form of Kissinger Eq. (19):

$$ln\left[\frac{\beta}{T^2}\right] = ln\left[\frac{AR\gamma}{Eg(\alpha)}\right] - \frac{E}{R}\frac{1}{T} \tag{19}$$

where: $\gamma = E/(E + 2RT)$

Equation (19) represents the FD formula of reaction rate which is the equation of a straight line whose slope is $(-E/R)$ and enables determining activation energy for the degree of conversion α. The frequency factor A of the Arrhenius equation can be calculated from the value of the free term. The relationship between heating rate β and temperature at a defined degree of conversion α is given by Eq. (20):

$$\ln[\beta] = ln\left[\frac{AR\gamma}{Eg(\alpha)}\right] - \frac{E}{R}\frac{1}{T} - 2ln\left[\frac{1}{T}\right] \tag{20}$$

when $\ln[\beta]$ is treated as a continuous variable and Eq. (19) is differentiated with respect to $1/T$, assuming that $\gamma = E/(E + 2RT)$ is temperature-independent and its value is close to 1. We obtain the value of the analytical derivative AD (21):

$$\frac{d\ln[\beta]}{d(1/T)} = -\frac{E}{R} - 2T \tag{21}$$

Equation (20) is analogous to the Flynn/Wall and Ozawa equations and also enables determining activation energy based on the slope of the line.
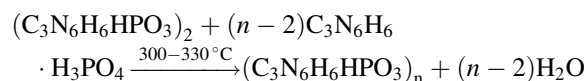
Experimental

Raw materials used for obtaining melamine polyphosphate are phosphoric acid and melamine. The first stage of the process is the synthesis of melamine phosphate (MP). Thereupon, the product is subjected to thermal condensation. Melamine phosphate polycondensation proceeds in several steps. The first one (formation of pyrophosphate) takes place in the temperature range of 250–300 °C. The next step, carried out in the temperature range of 300–330 °C, is the obtaining of melamine polyphosphate of varying degree of condensation.

In this work, we studied the first and second stage of melamine phosphate condensation, namely:

- Condensation of melamine phosphate (MP) that leads to formation of melamine pyrophosphate (MDP), as illustrated by Eq. 2:

$$2C_3N_6H_6 \cdot H_3PO_4 \xrightarrow{250-300\,°C} (C_3N_6H_6HPO_3)_2 + H_2O$$
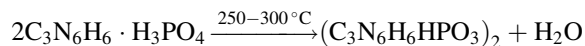
- Subsequent reaction of MDP to melamine polyphosphate (MPP), as illustrated by Eq. 3:

$$\begin{aligned}(C_3N_6H_6HPO_3)_2 &+ (n-2)C_3N_6H_6 \\ \cdot\, H_3PO_4 &\xrightarrow{300-330\,°C} (C_3N_6H_6HPO_3)_n + (n-2)H_2O\end{aligned}$$

by means of differential scanning calorimetry.

The yield of the polycondensation products are >99 %. Solubility in water at 20 °C polycondensation products are shown below: MP 0.7 g/100 g H_2O, MYPP 0.1 g/100 g H_2O, MPP 0.1 g/100 g H_2O. The temperatures of the polycondensation and decomposition of melamine phosphates are lower their melting points. Granulometric analysis of the raw materials (MP) presented in Table 1.

Mettler Toledo (Switzerland) DSC 822 differential scanning calorimeter was used. Thermal analyses were carried out in a dynamic atmosphere of air at a flow rate of 80 mL min^{-1}, in aluminum crucibles with a capacity of 40 μL. For calibration is used the standard—metallic indium. During calibration set, temperature of melting

Table 1 The particle size analysis of melamine orthophosphate

Percentage/%<	3	25	50	75	97
Size/μm	0.414	15.48	32.16	57.27	121.7

point (onset) is $T_{onset} = 156.42$ °C and enthalpy of melting is $H = -28.46$ J g^{-1}. The investigations were conducted under non-isothermal conditions. Temperature was changed linearly according to a set program (22):

$$\beta = \frac{dT}{dt} = const \qquad (22)$$

where β is the heating rate.

Five different heating rates were applied: 40, 20, 10, 5, 2 K min^{-1}.

The mass of each analyzed sample was ca. 3 mg. Previous studies [26] have indicated that for the significance level of $\gamma = 0.05$, no effect of the sample mass on the value of activation energy of the melamine phosphate condensation has been found within the tested range of mass (up to 10 mg).

An example of a DSC curve of melamine polyphosphate synthesis is shown in Fig. 1, and the characteristic
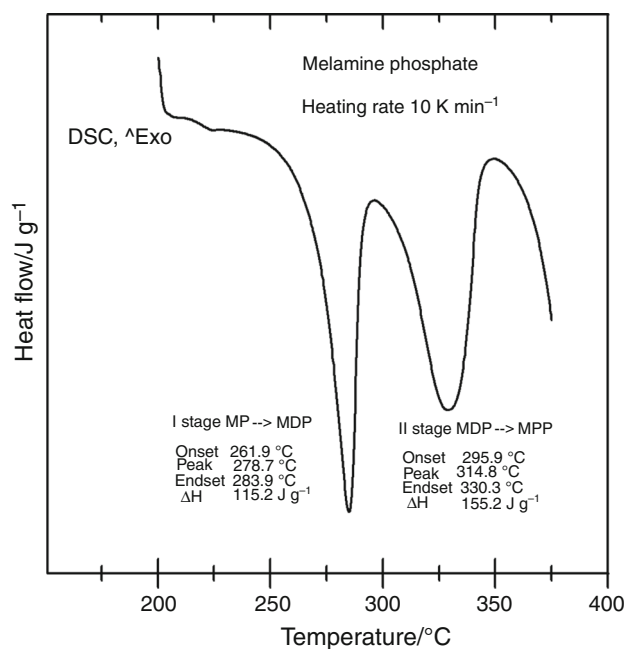

Fig. 1 DSC curve of thermal synthesis of melamine polyphosphate

parameters of the thermal decomposition for first and second stage of decomposition are listed in Table 2.

Approximate values of activation energy and of frequency factors were determined for both stages of condensation using the Kissinger method. Standard errors were calculated, and confidence intervals were determined by the t Student test for $\gamma = 0.05$, as in [26]. Table 3 lists the results obtained, and Fig. 2 presents a plot of the Kissinger equation. Equations 23 and 24 show Kissinger equation for stages I and II of polycondensation, respectively.

$$Y = -34.36\frac{1}{T_p} + 48.94 \qquad (23)$$

$$Y = -20.10\frac{1}{T_p} + 21.43 \qquad (24)$$

In order to acquire a better understanding of the reaction mechanism and to determine more accurate values of kinetic parameters of the process, the activation energy and the frequency factor were established using the isoconversional method. In this study, we used the Kissinger–Akahira–Sunose Eq. (16) for the determination of activation energy as a function of the degree of conversion. Calculations were made for 5 measurement series using different sample heating rates (from 40 down to 2 K min^{-1}). The dependence of the average activation energy on the degree of conversion α for both stages of polycondensation is shown in Fig. 3, and selected values along with error analysis are presented in Table 4. The adopted measure of error, as in above-described Kissinger method, was the standard error and the confidence interval at the significance level of $\alpha = 0.05$. Analysis was performed in the temperature range corresponding to the start (onset) and end (endset) of a given transformation. Lower intervals bear an excessively large relative error, and measurements in this range can adversely affect the results of kinetic calculations. At higher values of α, the contribution of the next polycondensation reaction or of the decomposition of the formed melamine polyphosphate becomes significant.

Table 2 The values of characteristic parameters of the thermal decomposition of melamine phosphate at various heating rates

Heating rate/K min^{-1}	Stage I of polyphosphate synthesis			Stage II of polyphosphate synthesis		
	T_{onset}/°C	T_{peak}/°C	ΔH/J g^{-1}	T_{onset}/°C	T_{peak}/°C	ΔH/J g^{-1}
2	250.0	265.3	113.8	278.2	292.6	169.6
5	256.2	271.9	118.6	287.2	303.9	163.5
10	261.9	278.7	115.6	295.9	314.8	155.2
20	268.7	285.0	119.6	307.4	328.7	149.4
40	280.0	290.3	117.5	323.4	340.3	155.0

Table 3 Values of activation energy and of frequency factors determined using the Kissinger method

Parameter	Stage I of polycondensation	Stage II of polycondensation
Activation energy,/kJ mol^{-1}	285.5 ± 8.49	167.0 ± 7.38
Confidence interval limits		
Lower/kJ mol^{-1}	258.5	143.6
Upper/kJ mol^{-1}	312.5	190.5
Frequency factor, ln(A)/ln(s^{-1})	58.3 ± 1.85	29.5 ± 1.51
Confidence interval limits		
Lower/ln(s^{-1})	52.4	24.7
Upper/ln(s^{-1})	64.2	34.3
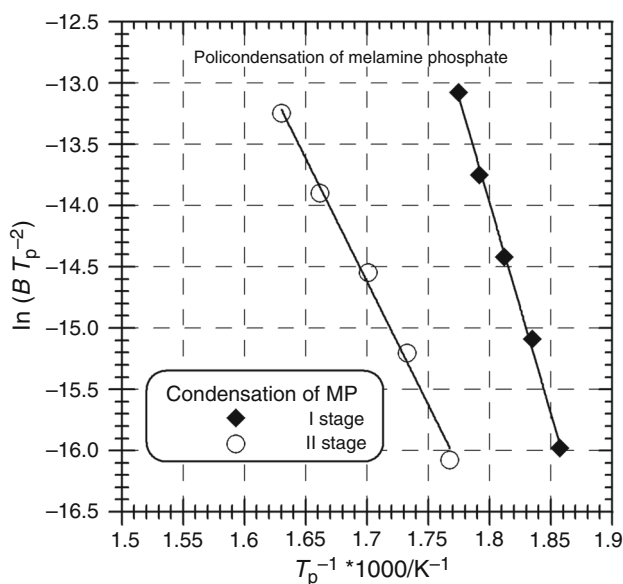
Fig. 2 Graphical interpretation of the Kissinger equation
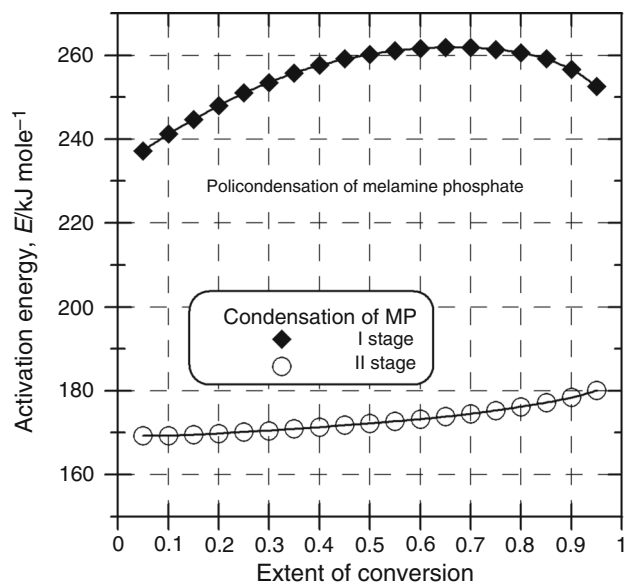
Fig. 3 Activation energy versus degree of conversion (Kissinger–Akahira–Sunose method)

Table 4 Activation energy at various degree of conversion calculated using the Kissinger–Akahira–Sunose isoconversional method

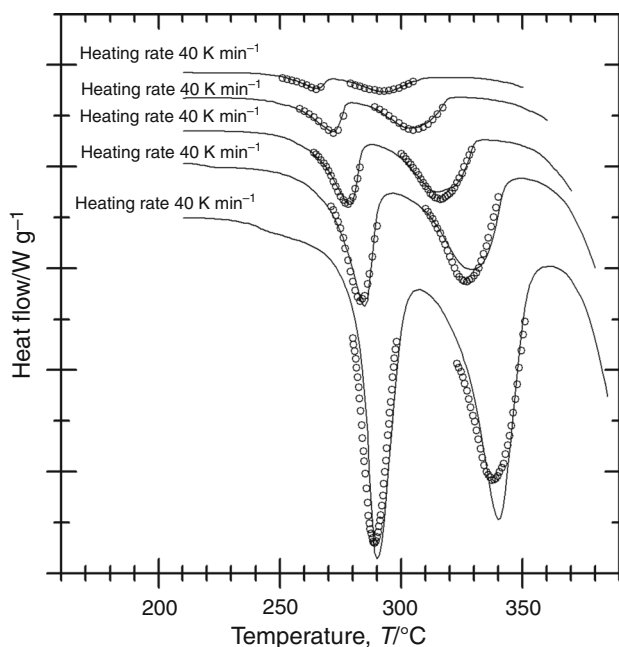|	Stage I of polycondensation extent of conversion, α				Stage II of polycondensation extent of conversion, α			
	0.05	0.25	0.50	0.75	0.05	0.25	0.50	0.75
Activation energy, E/kJ mol^{-1}	237.2	251.0	260.2	261.4	169.3	170.2	172.2	175.3
Standard error	±21.3	±15.4	±11.9	±10.2	±11.4	±7.72	±4.97	±4.48
Confidence interval limits								
Lower/kJ mol^{-1}	169.5	201.8	224.2	228.8	132.9	145.6	156.4	161.0
upper/kJ mol^{-1}	305.0	300.1	296.2	294.0	205.6	194.7	188.1	189.6
Frequency factor, ln(A)/ln(s^{-1})	48.6	51.2	52.9	52.9	30.7	30.4	30.5	30.9
Standard error	±4.73	±3.40	±2.37	±2.23	±2.38	±1.59	±1.02	±0.91
Confidence interval limits								
Lower/ln(s^{-1})	33.5	40.4	45.0	45.8	23.1	25.4	27.3	28.0
Upper/ln(s^{-1})	63.7	62.0	60.8	60.0	38.2	35.5	33.8	33.8

Fig. 4 Comparison between computed kinetic curves and experimental data. *Solid line*—experimental data, *circles*—simulated curves

The computed values of activation energy and of preexponential factor allowed to plot the theoretical kinetic curves which were then compared to actual experimental data. Comparative graphs for various heating rates are presented in Fig. 4. Solid line indicates the experimental data and circles—simulated curves. Discrepancies between calculated values and experimental data are shown in Table 5.

The fitting of a reaction model

The next step in the analysis of melamine phosphate polycondensation kinetics was the attempt to find a best-fit kinetic equation based on the collected kinetic data. The reaction model fitting method was used to find $f(\alpha)$ that best approximated the dependence of process rate on temperature and degree of conversion. We also determined the kinetic parameters of the process, namely activation energy E and pre-exponential frequency factor A [the reaction mechanism-dependent constant in Eq. (7)], together with theirs standard error values. The confidence interval for activation energy at the significance level of $\gamma = 0.05$ was also determined. The results obtained are listed in Table 6.

The best-fit parameters of the kinetic equations were determined by the method of combining linear and non-linear regression. The first-order equation F1 (Mampel equation) (25) provided the best fit for the first stage of melamine phosphate polycondensation:

$$f(\alpha) = 1 - \alpha \tag{25}$$

Reaction rate equation takes then the following form:

$$v(t) = A\exp\left(-\frac{E}{RT(t)}\right) \cdot (1 - \alpha) \tag{26}$$

Table 5 Relative error of discrepancy between theoretical curves and experimental data

Heating rate/K min^{-1}	Relative error of discrepancy between theoretical curves and experimental data	
	Stage I of polycondensation/%	Stage II of polycondensation/%
2	1.27	2.42
5	6.11	6.31
10	7.57	10.86
20	10.10	12.66
40	18.16	8.95

Table 6 Values of activation energy and of frequency factor determined using the reaction model fitting method

Value Kinetic model	Stage I of polycondensation $f(\alpha) = 1 - \alpha$	Stage II of polycondensation $f(\alpha) = 2(1 - \alpha) \cdot [-\ln(1 - \alpha)]^{1/2}$
Activation energy, E/kJ mol^{-1}	292.3 ± 6.43	173.2 ± 5.27
Confidence interval limits		
Lower/kJ mol^{-1}	271.8	156.4
Upper/kJ mol^{-1}	312.8	190.0
Frequency factor, $\ln(A)/\ln(s^{-1})$	51.6 ± 1.22	28.8 ± 1.15

The second stage of melamine phosphate conversion is best described by the Avrami-Erofeev A2 Eq. (27):

$$f(\alpha) = 2(1 - \alpha) \cdot [-\ln(1 - \alpha)]^{1/2} \tag{27}$$

and consequently the reaction rate equation has the form (28):

$$v(t) = A\exp\left(-\frac{E}{RT(t)}\right) \cdot 2(1 - \alpha) \cdot [-\ln(1 - \alpha)]^{1/2} \tag{28}$$

Summary and conclusions

This paper presents the results of study of the kinetics of two-stage condensation of melamine orthophosphate (MP) to melamine pyrophosphate (MDP) and subsequently to melamine polyphosphate (MPP). The activation energy of the process was determined using the approximate Kissinger method, the isoconversional Kissinger–Akahira–Sunose method and by developing a complete kinetic model.

Calculations made using the isoconversional Kissinger–Akahira–Sunose method confirm that the thus determined activation energy depends largely on the extent of conversion. This proves the complexity of the mechanism of the analyzed two-stage condensation. A complete analysis of the process was conducted to establish a kinetic model and determine the activation energy and the value of the pre-exponential factor. The reaction rate of the first stage of condensation is best described by a first-order reaction equation F1 (Mampel equation), while that of the second stage by the Avrami-Erofeev equation A2. For the first stage of condensation, the activation energy was determined in the range 250–300 °C; for second stage, the activation energy was determined in the range 300–330 °C. Kinetic parameters obtained from TG/DTG curves, presented in previous work, were related only to the first reaction stage of melamine polyphosphate synthesis. In this work, we investigated stages I and II. In the previous work, it was found that in the initial period of the conversion (up to the value of ca. 0.20), the limiting stage of the process is chemical reaction (first-order reaction model—Mampel F1 equation). At conversion values above 0.2, the reaction is described by Avrami–Erofeev A2 model. The activation energy depending on the method of calculation was approximately 250 kJ mol^{-1} and decreased with increasing extend of conversion. In the present work, calculated activation energy was also high (260–290 kJ mol^{-1}). In this case, function F1 had also the best fit.

The results presented here are a fragment of a wider laboratory- and industrial-scale research on developing method of production of melamine phosphate flame retardant. On the basis of the kinetic data and on the basis of other thermal tests will be developed temperature program preparation of melamine phosphate with varying degrees of polycondensation. The developed method will be verified in pilot scale.

The obtained results will help design heating appliances for the polycondensation process. Determined herein kinetic parameters of the reaction of melamine pyrophosphate (MDP) and melamine polyphosphate (MPP) synthesis may prove useful in the analysis of other polycondensation reactions of phosphoric acid derivatives. They may also be helpful when comparing the results of research on other condensation processes accompanied by release of water, both when using the reaction model fitting method and the isoconversional methods.

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