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New aspects on the mechanism of the solid state polyamidation of PA 6,6 salt

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Abstract

Hexamethylenediammonium adipate (PA 6,6 salt) was solid state polymerized in the temperature range of 158–190 °C, in a thermogravimetric analysis (TGA) chamber, which simulates a polyamidation reactor. A mechanism based on the role of the volatile component of the salt (i.e. hexamethylenediamine) is found to predominate: the diamine escapes along with polycondensation water, meanwhile this volatilization occurs earlier than the water formation, apparently resulting in an increase of the vacancy defects and of the nucleation sites in the salt crystals. In addition, critical reaction parameters, such as reaction time, temperature, surrounding gas and presence of catalyst in the starting material were investigated, so as to discern the rate-controlling mechanism of the process. Finally, proper SSP kinetics were studied taking into consideration the diamine loss occurred and SSP rate constants were calculated through a suitable rate expression.

Keywords: Nylon 6,6 salt; Solid state polymerization; Thermogravimetric analysis

1. Introduction

Solid state polyamidation (SSP) is widely used as an extension of the melt polymerization process, in order to produce high-molecular-weight resins. It involves heating the starting material (prepolymer) in an inert atmosphere at a temperature well above its glass transition point, but below melting temperature, resulting in a substantial increase in the degree of polymerization, while the material retains its solid shape [1,2]. Alternatively, 'direct' solid state polyamidation starting from dry hexamethylenediammonium adipate (PA 6,6 salt) has been studied using different techniques [3–8] and presents considerable practical interest, since all the problems associated with the high temperature of melt technology are avoided [3].

Regarding direct SSP mechanism, it is generally supported that it follows the nucleation and growth model [9]. As an example, Frayer et al. [10] proposed that the polymerization could be considered to consist of two stages, initiation and propagation. The initiation or nucleation stage can occur either on the surface of the crystallites or at internal surfaces within the crystallites. Similar is the picture from Macchi et al. [11] who heated single crystals of 6-aminocaproic acid and found that the kinetics of the process were characterized by three stages: an induction period, a stage in which monomer disappears at a constant rate and a slow polycondensation of the polyamide chains after exhaustion of the monomer. In addition, another mechanism has been also proposed by Papaspyrides [3,4], according to which the water produced during the solid state polycondensation reaction hydrates the polar groups of the reactant and, as the amount of water increases, the crystal structure of the salt is destroyed by the formation of highly hydrated regions. These areas have lower melting points and soon fall in the melt state, resulting in the experimentally observed transition of the reaction from the solid to the melt state (SMT phenomenon). As the reaction proceeds further, the molecular weight increases, the hygroscopicity of the reacting system decreases and finally the solid character of the system is restored. Thus, in direct SSP, the monomer is transformed into polymer by a reaction, which rarely takes place in a real solid state, depending on the reaction conditions and on the polyamide structure.

A large number of parameters are reported to affect the SSP overall rate and define the relevant rate-determining step,

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which may be the chemical reaction, the reactive chain end mobility and/or the condensate removal through diffusion. Reaction temperature emerges in many cases as the most important reaction factor. The higher the temperature, the shorter is the first stage of the SSP reaction, namely nucleation, above which the polymerization rate increases more intensively [12,13]. In addition, by-product diffusion limitations may occur during SSP process and this effect is generally more intense at high operating temperatures, where the chemical reaction is no longer the controlling step [14–16]. The effect of by-product diffusion may be concluded when investigating the reacting particles size and the flow rate of the inert gas. In the case of monomers SSP, the size of the crystals of the reacting mass is rather disregarded by most researchers. However, it was found that its effect is significant for grain sizes only below 20–25 mesh [17]. On the other hand, the surface by-product diffusion is mainly influenced by the flow of the inert gas [18] and in many cases, at low flow rates, the process is found to be diffusion-controlled.

Finally, the presence of catalysts in the preparation of polyamides has an accelerating effect on the rate of polymerization in both solid and melt phase reactions. The disadvantages of SSP are mainly overcome with the use of catalysts, which aim to increase the reaction rate and avoid particles agglomeration [7]. Therefore, acidic, basic and neutral compounds have been examined for their catalytic action. In the case of acid catalyzed polyamidation, the mechanism proposed involves the following equilibria [19]:

$$\text{–COOH} + \text{H}^+ \leftrightarrow \text{–COOH}_2^+ \tag{1}$$

$$\text{COOH}_2^+ + \text{H}_2\text{N–} \leftrightarrow \text{–CONH–} + \text{H}^+ + \text{H}_2\text{O} \tag{2}$$

For the SSP of PA 6,6 salt, reported catalysts used are: $H_3BO_3 > (COOH)_2 > H_3PO_4 > MgO$, meanwhile Na_2CO_3, $NaHSO_4$ and $(SiO_2)_n$ are proved to be inactive [8]. For polyoxamidation, compounds belonging to groups IVb and Vb of the periodic table of elements were found to act as catalysts: $SbF_3–As_2O_3 \gg GeO_2 > Sb_2O_3 > Bi_2O_3 \sim PbO$ [20].

In this paper, direct SSP is investigated in a small scale and the effect of a diffusion stage on the reaction mechanism is evaluated. The solid state polyamidation starting from dry PA 6,6 salt was performed in a thermogravimetric analysis (TGA) chamber, and critical reaction parameters were investigated, so as to discern the rate-controlling step regarding non catalytic and catalytic processes. New aspects on direct SSP emerge, since the volatile component of PA 6,6 salt (i.e. hexamethylenediamine) is proved to contribute significantly to the reaction mechanism, based on the nucleation and growth model.

2. Experimental

2.1. Starting material

Hexamethylenediammonium adipate (PA 6,6 salt) was supplied by Rhone–Poulenc Company. Boric acid (H_3BO_3) was used as a catalyst at a concentration of 1% w/w and was distributed within the starting material by dry mixing.

2.2. Solid state polymerization (SSP) runs

The SSP runs were carried out in a thermogravimetric analysis (TGA) chamber (DuPont 2100 thermal analysis). Small amounts of a salt sample (approximately 30 mg) were used as starting material. The SSP runs were first conducted at temperatures in the range of 160–190 °C under both dry-static and flowing (50 mL/min) nitrogen (Table 1).

A second series of SSP runs was carried out under flowing nitrogen at 158–189 °C and the TGA effluent gas was analyzed qualitatively by coupling an infrared spectometer (IR) to the TGA, in order to be able to monitor the evolution of HMD and water during polycondensation, when the temperature reaches the desired value. More specifically, based on the peak intensity in the IR spectra, the increase of each compound in the effluent gas was plotted against reaction time at constant temperature, using an arbitrary intensity scale. In addition, a titrator was coupled to the TGA so as to account quantitatively for the formation of H_2O and the loss of HMD.

The SSP progress was evaluated by continuous monitoring of the weight of the reacting mass, which was decreasing apparently due to the loss of polycondensation water. The latter is related to polymerization conversion (p_t) through Eq. (3), assuming stoichiometric equivalence of the end groups ($[NH_2]_0 = [COOH]_0$) in the starting PA 6,6 salt.

$$p_t = \frac{[NH_2]_0 - [NH_2]_t}{[NH_2]_0} = \frac{[H_2O]}{[NH_2]_0} \tag{3}$$

where, $[H_2O]$ is the concentration of polycondensation water (g equiv./kg), $[NH_2]_0$ the initial concentration of amine groups (g equiv./kg) and $[NH_2]_t$ is the concentration of amine groups at any given time (t) (g equiv./kg).

The weight loss (ΔW, g) at any given time during SSP is anticipated to be equal to the amount of polycondensation

Table 1
Experimental conditions of PA 6,6 salt SSP runs in the TGA chamber (160–190 °C)

Flowing N_2			Static N_2		
T (°C)	t (min)	$(\Delta W)_r$ (%)	T (°C)	t (min)	$(\Delta W)_r$ (%)
Non-catalytic runs					
162	1070	18.99	161	1275	19.69
173	400	19.38	172	692	19.10
177	324	19.08	176	350	18.89
178	238	18.27	180	356	19.02
190	200	19.05	185	220	18.12
			190	188	18.97
Catalytic runs					
160	1158	16.92	161	1100	16.58
169	744	17.16	172	892	17.06
175	312	16.94	177	896	18.04
179	208	16.96	180	282	16.76
190	190	17.36	190	190	17.26

The reduced weight loss $(\Delta W)_r$ of the reacting mass at the end of PA 6,6 salt SSP runs.

water, which escapes, and may be expressed as a function of polymerization conversion (p_t), of the initial concentration of amine end groups ($[NH_2]_0 = 7.62$ g equiv./kg) and of the amount of the reacting salt (m_t) at any given time expressed in kg (Eq. (4)).

$$\Delta W = 18 m_t [H_2O] = 18 p_t m_t [NH_2]_0 \qquad (4)$$

The theoretically weight loss at the end of the SSP reaction is calculated through Eq. (4), where polymerization conversion (p_t) is equal to 1. In addition, the 'reduced' weight loss, represented by $(\Delta W)_r$ and expressed in percent, is based on the initial weight of the sample (m_0 in kg). The rate ($\partial(\Delta W)_r/\partial t$) (in % per min) is the rate of the SSP reaction, assuming no hexamethylenediamine (HMD) loss. However, the latter assumption is hardly valid in the case of SSP reactions starting from the diamine–diacid salts, and therefore in most cases the aforementioned ratio indicates the rate of the decomposition of the starting material [6,8]. In each run, a TGA diagram is deduced, where the rate of weight loss is plotted in respect to the reaction time, including also the warming up period of the reacting mass.

3. Results and discussion

3.1. Main process parameters of PA 6,6 salt SSP

Direct solid state polymerization may play an important role in the polyamide production cycle. SSP starting from solid salt uses simpler technology, since the expensive removal of the water added prior to polymerization is avoided, and may contribute significantly in reducing the required energy consumption and in optimizing the quality of the end product, mainly due to the low operating temperatures.

Before examining the role of the main SSP parameters, it should be mentioned that transition to the melt state probably occurred during the runs, especially at the high reaction temperatures, e.g. at $T > 177$ °C. However, the SMT phenomenon could not be observed macroscopically, since there was no possibility of continuous monitoring of the physical form of the reacting mass. The latter is feasible when a glass assembly is used, as it was the case in a number of previous papers of Papaspyrides et al. [3–5,7], where the SMT phenomenon was clearly observed and investigated for the first time.

3.1.1. Hexamethylenediamine (HMD) volatilization phenomenon

Based on the results of PA 6,6 salt non-catalytic SSP runs shown in Table 1, the reduced weight loss $(\Delta W)_r$ at the end of all SSP runs varied between 18.12 and 19.69%, and it was thus found higher than the stoichiometric amount of water formed (13.72%) for polymerization conversion equal to 1 and for equimolar amounts of reactants (Eq. (4)). It becomes evident from the very beginning that the weight loss of the reacting mass during SSP was not only due to the removal of polycondensation water, but also to the volatilization of the hexamethylenediamine (HMD). The readily volatile diamine escaped along with water, as it has been already observed during the SSP of PA 6,6 and 6,10 salts [6,8] and also of different aromatic polyamide salts [21]. Several measures have been adopted during PA 6,6 production to treat HMD loss, such as the introduction of the diamine from the beginning of the polycondensation reaction in an amount sufficient to counteract diamine loss [22], the use of nitrogen gas containing HMD, and finally the decrease of the reaction temperature in order to minimize the HMD loss [23]. In addition, for the same reason, a two-step process has been proposed: first the reaction is carried out under autogenous conditions (pressurized system) to or beyond the point where diamine ends have reacted; subsequently the system is vented so as to remove the produced water and to drive the condensation reaction towards higher degrees of polymerization [24,25].

The HMD loss during SSP under flowing nitrogen was further studied by using IR spectroscopy. Accordingly, HMD and water were identified by IR analysis of the TGA effluent gas and their evolution was monitored throughout the SSP process at constant reaction temperature. It was then discovered that the diamine escaped earlier than polycondensation water. Regarding SSP at 180 °C, Fig. 1(a) shows that after the first 30 min of SSP, the diamine was detected and its quantity increased rapidly, reaching the highest value at the

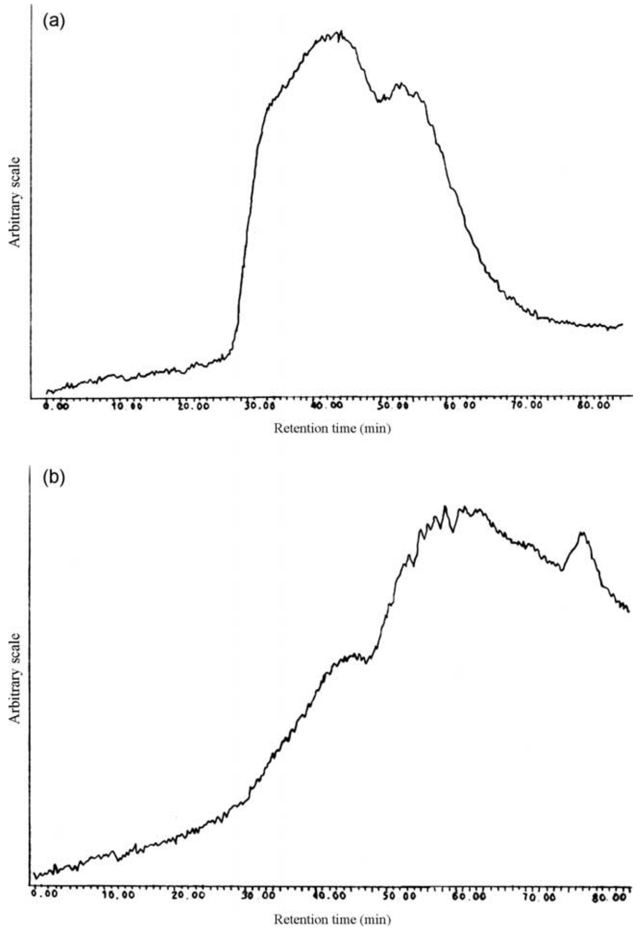

Fig. 1. Evolution of (a) HMD and (b) water during SSP of PA 6,6 salt at 180 °C under flowing nitrogen.

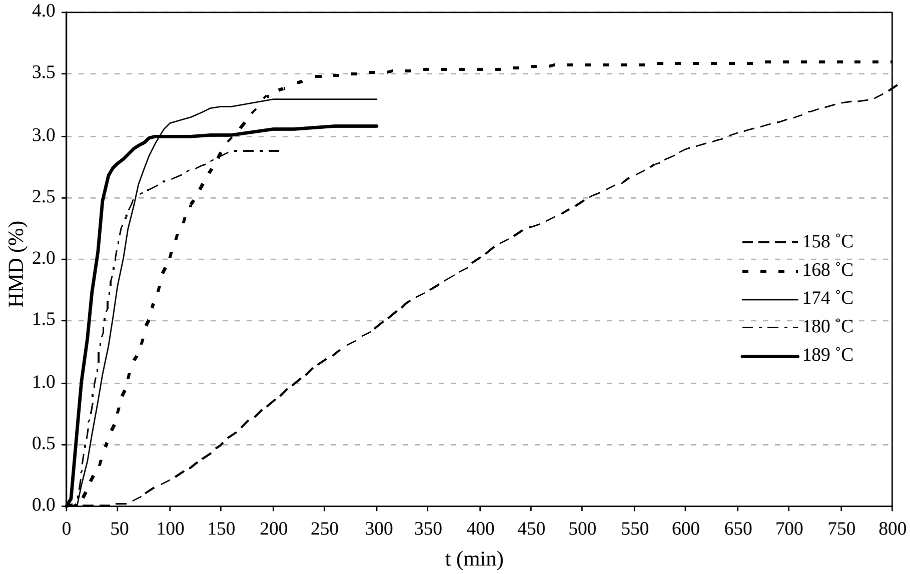

Fig. 2. Reduced weight loss due to HMD (%) during SSP of PA 6,6 salt under flowing nitrogen.

reaction time of 40 min. On the other hand, based on Fig. 1(b), the polycondensation water escaped at low rate during the first 50 min, after which the water loss was more intense and reached the highest value at 60 min. Thus, the HMD loss dominates early in the reaction; then, the reaction accelerates, as it is evident from the rapid increase in the water loss.

The quantitative characterization of the effluent gas verified the findings of IR analysis and the reduced weight loss ($(\Delta W)_r$ in %) due to HMD (Fig. 2) and to H_2O (Fig. 3) was plotted against reaction time and temperature. The reduced weight loss due to water formation remained below the theoretical value (13.72%), meanwhile the diamine loss varied between 2.8 and 3.7%. Based on the water weight loss and on Eq. (3), the polymerization conversion (p_t) was calculated through Eq. (5), where the amount of the reacting salt (m_t) decreases as a function of the amount of the escaped water and diamine (Eq. (6)).

$$p_t = \frac{m_{H_2O,t}}{18[NH_2]_0 m_t} \tag{5}$$

$$m_t = m_0 - 10^{-3} m_{H_2O,t} - m_{HMD,t} \tag{6}$$

where, $m_{H_2O,t}$ the amount of the water escaped at any given time (t) (g), $m_{HMD,t}$ the amount of the diamine escaped at any given time (t) (kg), m_0 the initial weight of the salt (kg) and $[NH_2]_0$ the initial concentration of amine ends (g equiv./kg).

Actually, through Eq. (6), the effect of the HMD volatilization on the polymerization conversion was considered at any given time. The deduced plots of p_t against time (Fig. 4(a)) show that the kinetics of the process were

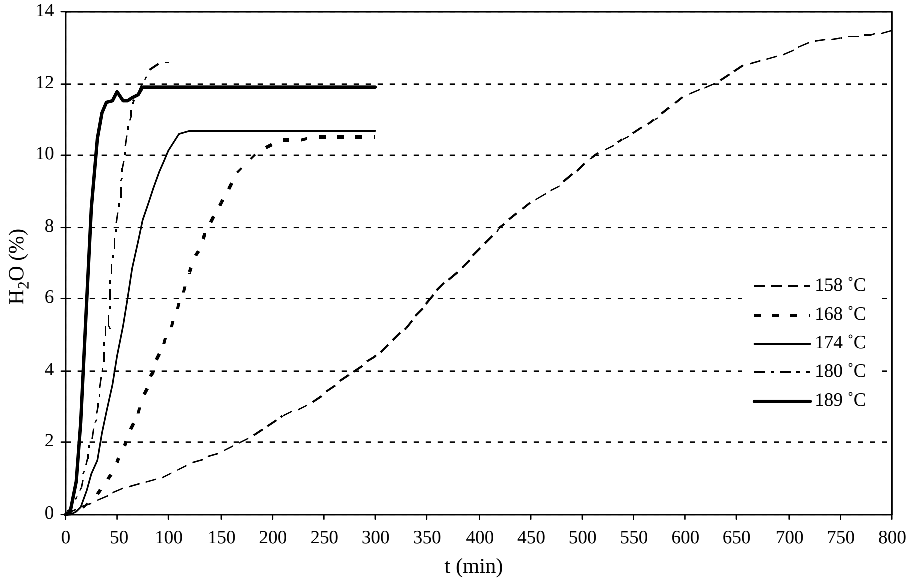

Fig. 3. Reduced weight loss due to H_2O (%) during SSP of PA 6,6 salt under flowing nitrogen.

characterized by two stages, namely induction and propagation, and these S-shape curves at each reaction temperature are indicative for the nucleation-growth model [10,12]. More important, at 180 °C, the duration of the nucleation stage (40 min) (Fig. 4(b)) coincides with the HMD loss, as observed in Fig. 1(a).

Combining the early evolution of HMD, as observed through IR analysis, and the theory of the nucleation-growth model, which seems to prevail based on the two-stage character of the process (initiation–propagation), an SSP mechanism may be suggested. According to the nucleation-growth model, the crystal lattice and its characteristics, such as the size of the crystals, the number and the type of lattice defects and the presence of impurities, may influence significantly the polymerization in the solid state. For instance, crystal edges and defects may in some cases inhibit the propagation of polymerization through physical separation of the polymerizing units, while in other cases they may act as active centers, since the orientation of the reacting species at the defective surfaces within the crystallites may differ and promote the nucleation of the polymer phase (initiation stage). Impurities may act by creating lattice defects, which subsequently affect polymerization, may act as a physical diluent to impede polymerization or they may facilitate molecular mobility and assist the polymerization [9]. Based on these well known principles of solid state chemistry, the early evolution of HMD may be associated to the nucleation stage: the diamine volatilization results in creating new defective surfaces in the crystal lattice and in increasing the active centers for the nucleation of the generated polymer phase, which is further grown following water formation.

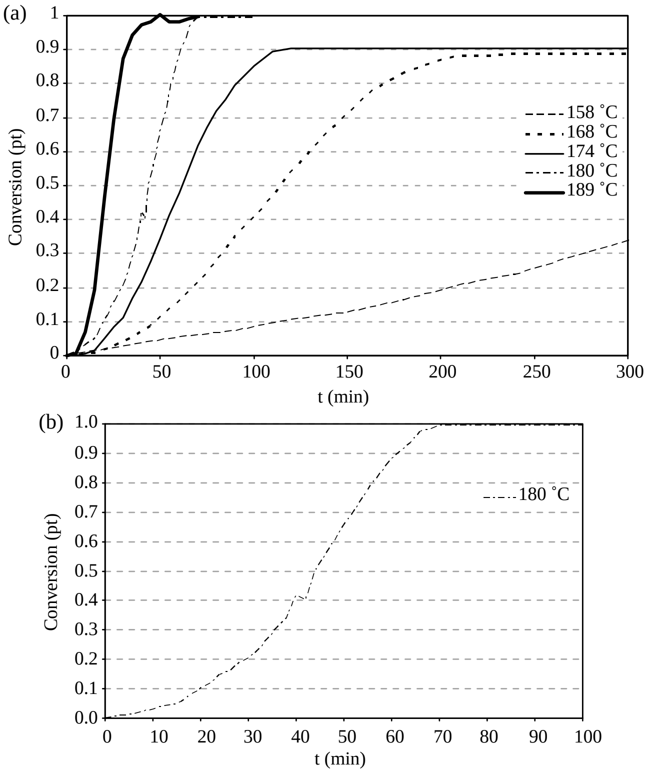

Fig. 4. (a) Polymerization conversion (p_t) vs. reaction time and temperature during SSP of PA 6,6 salt under flowing nitrogen. (b) Conversion (p_t) vs. reaction time at 180 °C.

3.1.2. The effect of reaction temperature

Turning to the SSP rate parameters, Fig. 4(a) combined with the change of the weight loss of the reacting mass under flowing (Fig. 5) and static nitrogen (Fig. 6), revealed that the temperature is the most important direct SSP variable. Specifically, higher rates of weight loss were attained sooner at elevated reaction temperatures as is shown by both the sharpness of the rate of weight loss curves and their duration, including also the warming up period. The sharper the rate of weight loss and the shorter their duration, the faster are the kinetics of the polymerization. At the low temperature of 161–162 °C, polymerization hardly occurred. The rate of weight loss curve becomes much sharper at 173 °C and it reaches its sharpest and faster response at 190 °C, verifying that there is an efficient, narrow temperature range for SSP reaction close to the melting point (191–192 °C) of the starting material, as stated already in previous studies [26]. It is interesting to note that, when comparing the rates of $(\Delta W)_r$ at 190 and 173 °C under flowing nitrogen, the reduced weight loss rate was increased by 225% with each 10 °C temperature increment.

3.1.3. The effect of the surrounding gas

The influence of the surrounding gas on the weight loss rate was also examined. In the non-catalytic runs, the latter was found to be higher when using flowing nitrogen instead of static. As an example, at 177 °C (Fig. 7), the rate of the reduced weight loss was increased by 69%, when using flowing nitrogen vs. static nitrogen atmosphere. Indeed, it is a well-known fact that an increase in the nitrogen flow rate not only increases the mass and heat transfer rates in the gas–solid system, but also reduces the by-product concentration in the gas phase and accelerates its diffusion from the particle surface into the bulk of the gas phase [10,18]. In addition, the increase in the rate of nitrogen flow may favor the aforementioned diamine volatilization process and result in a higher number of nucleation sites. In overall, the pure PA 6,6 salt SSP process

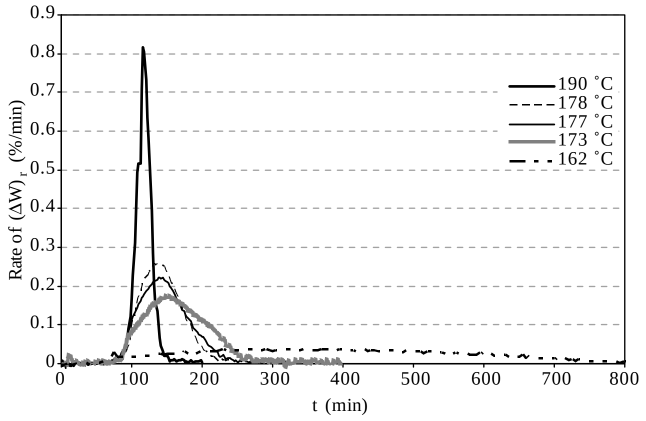

Fig. 5. Rate of the reduced weight loss ($\partial(\Delta W)_r/\partial t$) of the reacting mass during SSP of PA 6,6 salt under flowing nitrogen.

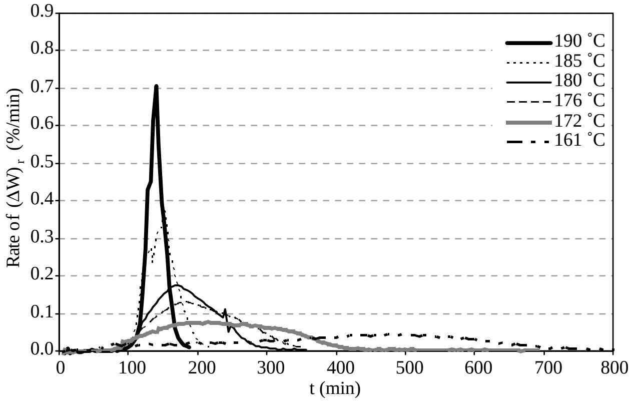

Fig. 6. Rate of the reduced weight loss ($\partial(\Delta W)_r/\partial t$) of the reacting mass during SSP of PA 6,6 salt under static nitrogen.

and/or the volatilization of HMD may be thus considered as diffusion-controlled, and the diffusion limitations predominate especially at the higher reaction temperatures [14–16].

3.1.4. The effect of catalyst

Regarding the catalytic runs, the effectiveness of boric acid (H_3BO_3) as a catalyst in the PA 6,6 salt SSP was also proved here (Fig. 8). The highest rate of weight loss was attained sooner when using boric acid (114 min) in comparison to the non-catalytic run (140 min). The process was accelerated and the positive effect of reaction temperature was also verified in the catalytic runs under both flowing and static nitrogen (Figs. 9 and 10).

Finally, in the catalytic runs, the process-limiting step was no longer the diffusion, since there was no difference in the rate of the reduced weight loss under either flowing or static nitrogen (Fig. 11), as it was in the non-catalytic case (Fig. 7). In other words, it seems that boric acid contributes in changing the reaction mechanism and favors the diffusion stage, which is not any more the slower process step. This finding is consistent with the Papaspyrides' mechanism mentioned in Section 1, which indicates the significant role of polycondensation water. More specifically, previous PA 6,6 salt SSP data [5] prove that, in the presence of catalysts, no water accumulation (or trend towards that) occurred, and the transition observed from the solid to the melt state (SMT phenomenon) was inhibited. The suggested catalysis mechanism was thus based on the easier removal of the water formed, away from the reacting sites, and on the restriction of the hydration of the salt structure. The findings of this paper, regarding the change of the reaction controlling step in the presence of a catalyst, verify the aforementioned catalysis mechanism, since the process is no longer diffusion-controlled, i.e. the diffusion of the water and/or HMD through the particle to the surrounding gas is favoured, so that the nucleation stage becomes shorter and the reaction equilibrium is shifted to the right.

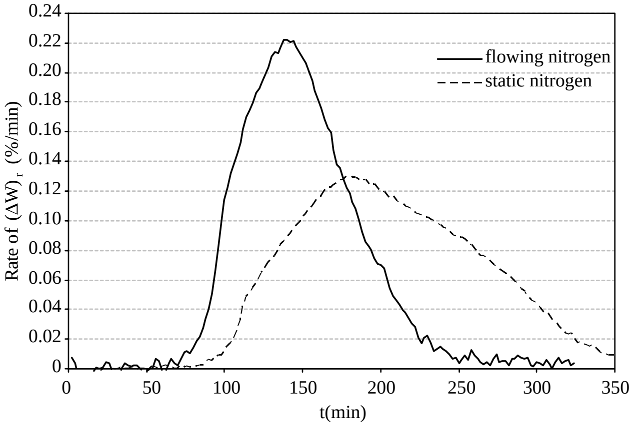

Fig. 7. Rate of the reduced weight loss ($\partial(\Delta W)_r/\partial t$) of the reacting mass during the SSP runs of PA 6,6 salt under flowing and static nitrogen at 177 °C.

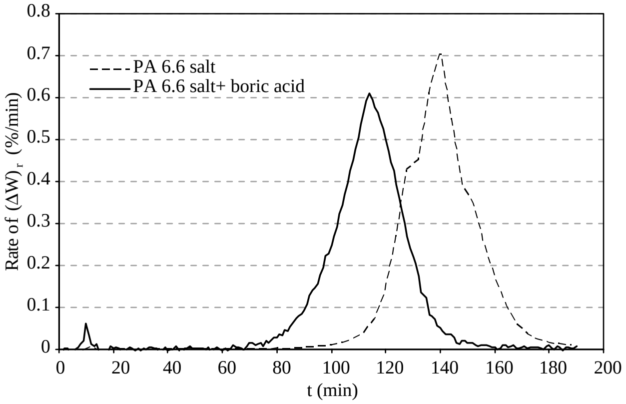

Fig. 8. Rate of the reduced weight loss ($\partial(\Delta W)_r/\partial t$) of the reacting mass during non-catalytic and catalytic SSP runs of PA 6,6 salt at 190 °C under static nitrogen.

3.2. PA 6,6 salt SSP kinetics

The kinetics of solid-state polyamidation starting from pure PA 6,6 salt and under flowing nitrogen were also investigated. The observed HMD volatilization apparently reduces the reaction rate, due to the disturbance caused in the stoichiometric equivalence of the functional end groups [6,8], and also impedes the proper kinetics study of the process [26]. More specifically, the technique applied here, i.e. coupling the TGA with a titrator, permits for the first time a reliable kinetics study, since the concentration of the water formed was

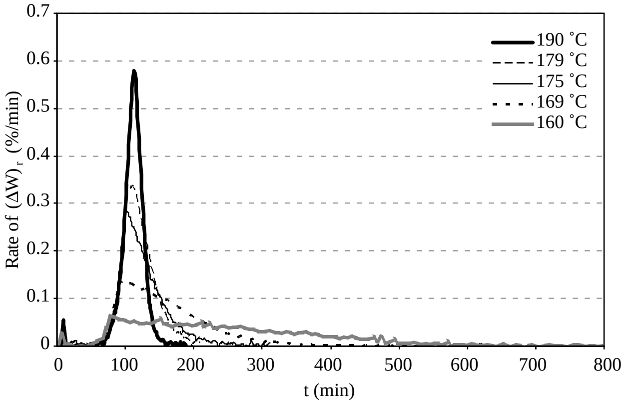

Fig. 9. Rate of the reduced weight loss ($\partial(\Delta W)_r/\partial t$) of the reacting mass during SSP runs of PA 6,6 salt with boric acid under flowing nitrogen.

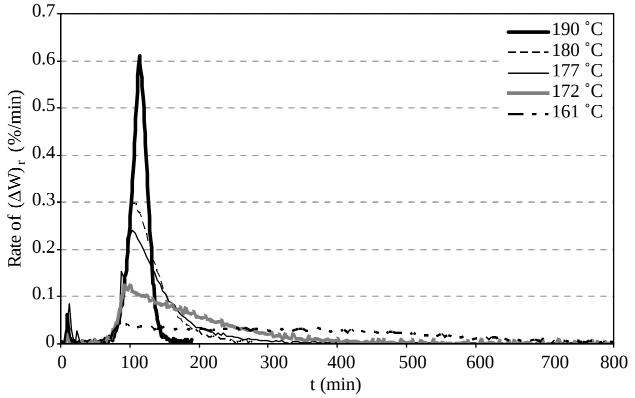

Fig. 10. Rate of the reduced weight loss ($\partial(\Delta W)_r/\partial t$) of the reacting mass during SSP runs of PA 6,6 salt with boric acid under static nitrogen.

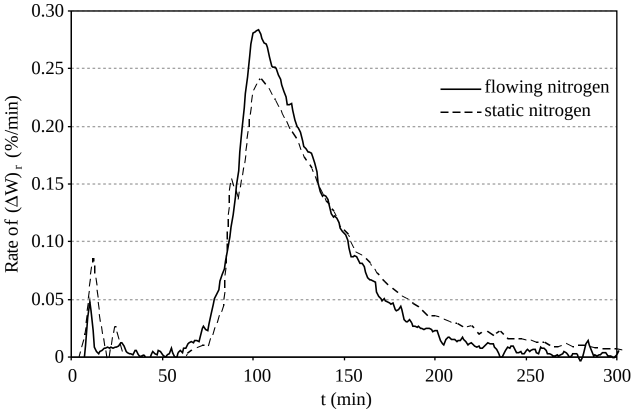

Fig. 11. Rate of the reduced weight loss ($\partial(\Delta W)_r/\partial t$) of the reacting mass during SSP catalytic runs at 177 °C under flowing and static nitrogen.

correctly estimated (Fig. 3), taking into account the separation of the volatile diamine (Fig. 2).

According to Flory's theory [27], the SSP rate can be described by either second- or third-order kinetics in respect to the end group concentrations. Third-order kinetics indicate that one of the functional groups exhibits catalytic behavior, and thus its effect on polymerization must be included in the rate equation. On the contrary, the second-order kinetics refers to acid catalyzed polymerizations, where the concentration of the catalyst is included in the rate constant k_2. In our case, both Flory rate expressions were tested by fitting the end goup concentration data (Eqs. (7) and (8)), but they failed to describe the process for the pure PA 6,6 salt SSP under flowing nitrogen.

$$[\mathrm{COOH}]_t = [\mathrm{COOH}]_0 - [\mathrm{H_2O}]_t \tag{7}$$

$$[\mathrm{NH_2}]_t = [\mathrm{NH_2}]_0 - [\mathrm{NH_2}]_{\mathrm{lost}} - [\mathrm{H_2O}]_t \tag{8}$$

where, $[\mathrm{COOH}]_t$ and $[\mathrm{NH_2}]_t$ the concentrations of the carboxyl and amine end groups (g equiv./kg) at any given time (t), $[\mathrm{COOH}]_0$ and $[\mathrm{NH_2}]_0$ the initial concentrations of the carboxyl and amine end groups (g equiv./kg), $[\mathrm{NH_2}]_{\mathrm{lost}}$ the concentration of amine end groups (g equiv./kg) which are lost due to the volatilization of HMD at any given time (t), $[\mathrm{H_2O}]_t$ the concentration of water formed (g equiv./kg) at any given time (t).

On the grounds that the pure PA 6,6 salt process was found diffusion-controlled (Fig. 7), the SSP rate may be expressed as some power of reaction time. The below quoted equation consists of a typical power-law model, implying that the current SSP reaction is jointly controlled by chemical reaction and diffusion [28,29].

$$\text{rate} = \frac{\mathrm{d}[\mathrm{H_2O}]}{\mathrm{d}t} = kt^n \xrightarrow{\int} \ln[\mathrm{H_2O}] = \ln([\mathrm{NH_2}]_0 p_t)$$

$$= \ln\frac{k}{n+1} + (n+1)\ln t \tag{9}$$

where, n the power of the time and k the rate constant in (g equiv./kg)min^{-n-1}.

Eq. (9) was tested by fitting our experimental data (Figs. 2 and 3) at each reaction temperature using Eqs. (5) and (6):

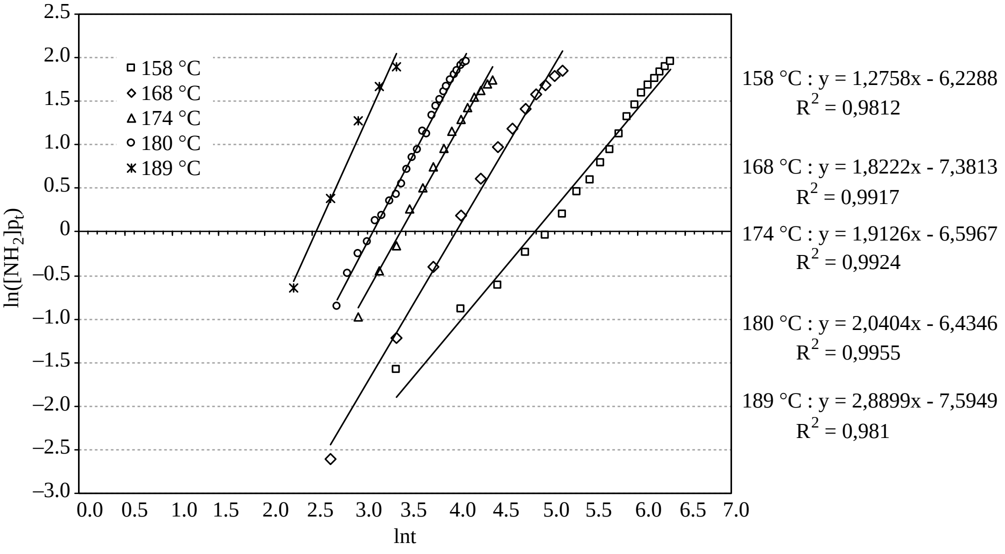

Fig. 12. Fitting of the power-law model (Eq. (9)) to the experimental data of pure PA 6,6 salt SSP under flowing nitrogen.

Table 2
Reaction order (n) and rate constants (k) for the SSP of pure PA 6,6 salt under flowing nitrogen (158–189 °C)

T (°C)	n	k
158	0.2758	0.0025 (g equiv./kg)$\mathrm{min}^{-1.2758}$
168	0.8222	0.0011 (g equiv./kg)$\mathrm{min}^{-1.8222}$
174	0.9126	0.0026 (g equiv./kg)$\mathrm{min}^{-1.9126}$
180	1.0404	0.0033 (g equiv./kg)$\mathrm{min}^{-2.0404}$
189	1.8899	0.0014 (g equiv./kg)$\mathrm{min}^{-2.8899}$

$\ln([\mathrm{NH_2}]_0 p_t)$ vs. $\ln t$ was plotted so as to determine the power (n) of the time from the line slope ($n+1$) and the rate constant from the intercept ($\ln(k/n+1)$) at $\ln t=0$. It was found that this simple model describes indeed satisfactorily the overall process and fits adequately all data, based on the high correlation coefficients ($R^2=0.9810$–0.9955) (Fig. 12). The power of the time (n) and the rate constants (k) are shown in Table 2, where the n values were found to increase linearly ($R^2=0.9177$) with the reaction temperature (T) (Eq. (8)), showing probably the effect of the latter on the diamine diffusion step: as temperature increases, the HMD volatilization is favored, the nucleation stage is shortened and SSP is accelerated.

$$n = 0.0475T - 20.215 \tag{10}$$

where, T the absolute temperature in K.

Finally, combining Eqs. (9) and (10), Eq. (11) was deduced, where the polymerization conversion (p_t) can be calculated through a power-law model, where the effect of diamine loss is also included.

$$\ln p_t = (0.045T - 19.215)\ln t + \ln\frac{k}{0.045T - 19.215} - 2.03 \tag{11}$$

4. Conclusions

Solid state polymerization starting from dry PA 6,6 salt was investigated, by conducting the SSP runs in a thermogravimetric analysis chamber. In all cases, the volatile hexamethylenediamine escaped along with polycondensation water, disturbing the stoichiometric equivalence of the functional end groups. Coupling TGA with both IR analysis and titration was used for the first time successfully to account qualitatively and quantitatively for the formation of water and the loss of diamine, permitting thus a reliable kinetics study. Specifically, it was shown that the diamine loss dominates early in the reaction, after which water is rapidly formed. This volatilization suggests an SSP mechanism, according to which new defective surfaces are created in the salt crystal lattice, being appropriate for the nucleation of the polymer phase. Furthermore, the reaction behavior in catalytic runs was studied and it was found that the presence of catalyst changes the controlling mechanism, which is no longer the diffusion. Finally, based on the kinetics study, the diffusion-controlled character of the pure PA 6,6 salt process was verified, since the rate of the polycondensation was satisfactorily described as some power of reaction time.

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