Solid state polyamidation of nylon salts:possible mechanism for the transition solid-melt

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Solid state polyamidation of nylon salts may be accompanied, depending on the reaction conditions, by a typical transition of the process from the solid to the melt state. For an explanation of this phenomenon, dodecamethylenediammonium adipate, a typical salt with such a transitional behaviour, has been chosen for further study. The possibility of the formation of an eutectic system monomer–polymer has been excluded and the role of the water of polycondensation has been taken into account. Water quantitative determinations proved that a significant amount of the water produced, during the course of the reaction, cannot be removed out of the reacting grains. Due to the deliquescent behaviour of the monomer, it is proposed that this water accumulation results in the formation of lower melting point areas. Overlapping of the latter explains the transition observed.

(Keywords: dodecamethylenediammonium adipate; solid state polyamidation; solid-melt transition; water accumulation)

INTRODUCTION

In a previous paper from this laboratory[1] the effect of the reaction temperature on the solid state polyamidation (SSP) of the dodecamethylenediammonium adipate (DMA) has been thoroughly studied. The reaction proceeds at a marked rate in a temperature range extending up to about 25°C below the melting point of the salt. However, even at the lower temperatures of this range, the reaction turns from the solid to the melt state resulting in a fast agglomeration of the reacting grains.

Solid–melt transition has previously been referred to in the literature, both for nylon salts and aminoacids polymerized in the solid state. Volokhina *et al.*[2], studying the SSP of the aminoenanthoic acid, pointed out that in the presence of catalysts the reaction rate is accelerated, but eventually the process turns from the solid to the melt state. The same phenomenon was also observed[3] when the study was extended to the non-catalysed SSP of nylon salts based on *cis*-hexahydroxyterephthalic acid. Furthermore, Monroe[4] in a patent concerned with the solid phase polymerization of nylon salts, such as the hexamethylenediammonium adipate (HMA), described the transition clearly. Even by using prepolymer as a raw material, there exists a temperature range in which the polymerizing particles tend to agglomerate by sticking to one another. More recently, in a couple of papers from our laboratory, a distinct transition solid–melt has been referred to during the course of the non-catalysed SSP of the hexamethylenediammonium maleate[5] and also during the course of the catalysed, in addition to the non-catalysed, SSP of the DMA[6]. Nevertheless, none of the above mentioned papers provides an explanation of the phenomenon noticed. However, it has been proposed that the SSP reaction mechanism is not unique in prevailing continuously during the overall polyamidation process. In fact, in addition to our conclusions[1], Dasgupta[7] studying the SSP of HMA has pointed out that at 160°C the reaction followed zero order kinetics up to a conversion of $22 \pm 2\%$, whereas beyond this conversion the polymerization followed second order kinetics. Similar results have also been presented by Khripkov *et al.*[8] who proposed that the SSP of HMA catalysed by boric acid consists of two stages obeying different kinetics. It seems possible that the reason for such a behaviour is the fact that the SSP may fall, or even approach the melt state, depending on the salt nature and the reaction conditions[9].

What is indeed surprising is that in a lot of studies concerning the SSP reaction mechanism[2–4,8,10–17] no role has been given to the water produced during the polymerization process. Nevertheless, in this paper an attempt is made to explain the observed transition of the DMA polyamidation from the solid to the melt state on the grounds of the water formed. This may significantly help in understanding the true reaction mechanism of the solid state polyamidation of nylon salts or aminoacids. The role of the water produced is seriously taken into account by quantitative water determinations during the course of the reaction. A physical model is proposed to satisfactorily explain the experimental data obtained.

EXPERIMENTAL

The stages of DMA preparation, polymerization and characterization have been thoroughly described[1], excepting the procedure followed for quantitative determination of the polycondensation water. The sample was taken out of the reactor, washed with n-hexane and dried in an oven at 60°C for 10 min. Subsequently the sample

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was dispersed in methanol and titrated with 'Karl Fischer' reagent[18].

RESULTS AND DISCUSSION

To study the solid-melt transition during the course of the DMA solid state polyamidation, attention was focused on the reacting salt grain. Excluding any contamination effects from the surrounded non-solvent, impurities, etc., two physical models were distinguished, both based on the role of the polycondensation water produced.

'Binary model'

According to the binary model, the role of the water produced is negligible. This supposition is fulfilled when the water, just after formation, is freely removed and the reacting mass remains with nearly zero water concentration. Nevertheless, independently of its concentration, the water is also supposed to be totally inert, i.e. with no physical or chemical action on the components of the reacting mass. Then, the latter could be considered as a binary system, consisting simply of DMA monomer and higher molecular weight product. If this is the case, an explanation for the transition observed should be based on the possibility of this binary system being an eutectic one. Solid–melt transition occurs when the melting point of the eutectic composition reaches the reaction temperature, i.e. the boiling point of the non-solvent employed. Accordingly, the following requirements should be experimentally confirmed:

(a) The existence of a distinct minimum should be evident in the melting point vs. composition curve. This minimum should be lower than the level of the reaction temperature, at which transition to the melt state occurs.

(b) A fixed value of composition should correspond to the minimum expected.

(c) In the melt state, the reacting material should be homogeneous, i.e. monomer and product of higher molecular weight should be completely compatible.

In order to check the requirement (a) the melting points of model mixtures of DMA salt and water-insoluble[1] polycondensation product were determined. The composition in salt was varied from 100% to 0% w/w and typical results obtained are given in *Figure 1*. As the curve indicates, the melting point takes its lower value (about 145°C) at a composition of ~60% w/w. Due to the fact that transition to melt has been observed at much lower temperatures[1], supposition (a) has to be rejected.

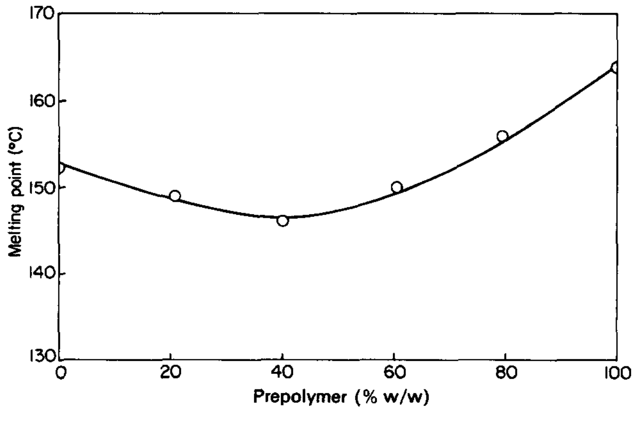

Figure 1 Melting point *versus* composition in prepolymer of [η]=11 ml/g(*m*-cresol, 37.7°C)

To examine whether the minimum melting point appeared corresponds to a fixed value of composition (requirement (b)), the DMA solid state polyamidation was repeated under different conditions, i.e. by varying the reaction temperature profile followed during the course of the process. In all cases a transition to the melt state took place and exactly at that time the water-insoluble fraction c_i' of the reacting mass was determined. The results obtained are given in *Table 1* whereas the kinetic curves of the reaction runs carried out are shown in *Figure 2*, together with the corresponding temperature profiles. It is evident that transition to the melt state corresponds to a wide area of composition extending from 18% to 42% w/w in water-insoluble component, i.e. in product of higher molecular weight. Therefore, supposition (b) has also to be rejected.

Supposition (c) was checked by both macroscopic and microscopic examinations of the reacting mass, after transition to the melt state. In all cases the melt was found to consist of a liquid phase in which a distinguished solid phase was dispersed.

According to the above experimental evidence none of the discussed requirements was proved valid and therefore the solid–melt transition observed cannot be due to an eutectic influence, i.e. the binary model considered should be rejected.

'Ternary model'

According to this model, an active role is given to the water produced during the course of the reaction, i.e. significant interaction with the monomer and/or polymer formed is not excluded. If this is the case, then the reacting material could be considered as a ternary system: monomer–polymer–water. DMA is readily soluble in water, even at room temperature, while nylon 12,6 is typically insoluble[1]. Accordingly, transition to the melt state could be explained by the formation of low melting point areas due to the action of the water on the monomer. At high water contents, favoured when all the polycondensation water cannot be removed out of the reacting grain, the monomer may be dissolved, whereas the higher molecular weight component, being insoluble, may comprise a second phase distributed within the monomer–water liquid phase.

To check this alternative supposition it was necessary to verify: (a) any influence of the water on the melting point of the salt; (b) any influence of the water on the melting point of the higher molecular weight product; (c) whether, within the temperature range used in SSP runs, nylon 12,6 of considerable molecular weight is compatible with DMA-water melts; and (d) any accumulation of the polycondensation water produced within the reacting grains.

The influence of the water on the melting point of the salt was easily verified as follows. Samples of DMA salt were conditioned at room temperature in air saturated with water vapour. In *Figure 3* the experimental curves of weight gain and melting point vs. conditioning time are shown. The highly hydroscopic nature of the DMA salt is revealed together with the strong influence on its melting point of the moisture absorbed. It is worth while to emphasize that after conditioning for less than 24 h all the samples used were completely liquefied. On the contrary, under the same conditions and for conditioning times exceeding a week, no influence was observed on the

Table 1 Water-insoluble fractions of samples taken out of the reactor exactly at the transition point to the melt state

Polymerization run	Water-insoluble fraction (c'_i)	Conversion (p)
1*	0.18	0.175
2	0.42	0.288
3	0.25	0.209

*Reference numbers indicated correspond to the kinetic curves of *Figures 2* (*a*, *b* and *c* respectively)

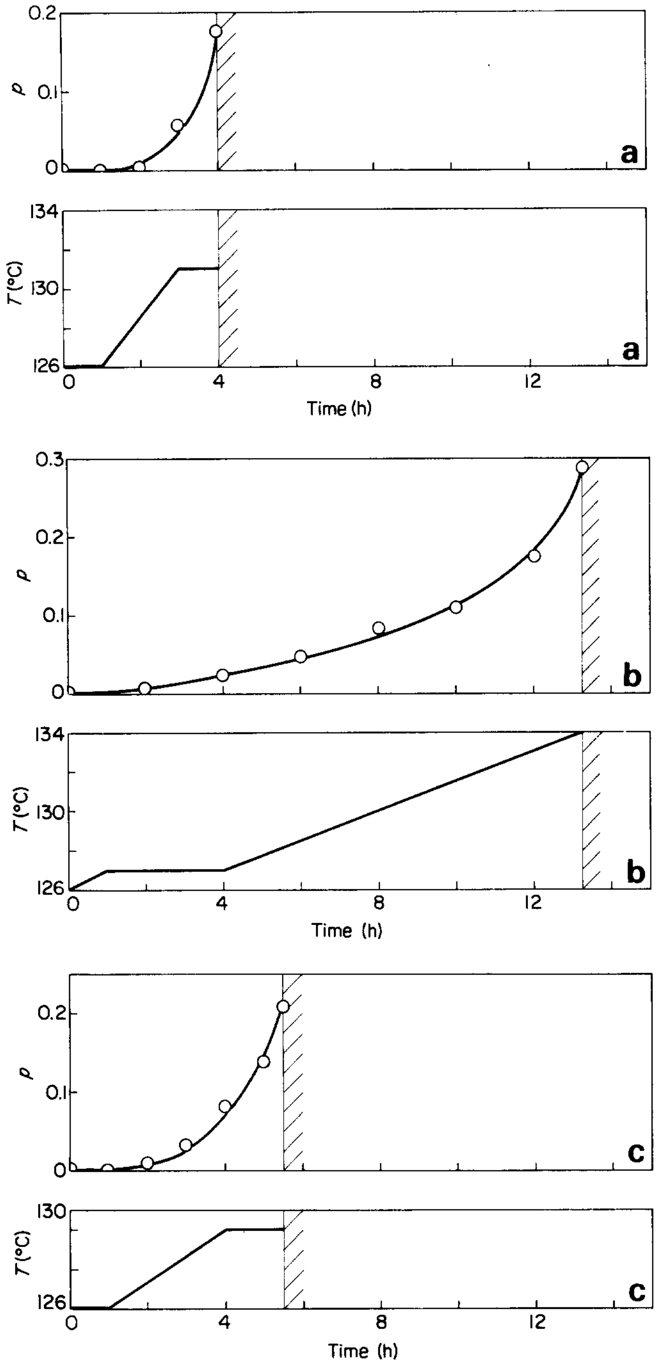

Figure 2 Plots of the conversion *p versus* time while varying the reaction temperature *T*. Shaded area indicates melt state

melting point of nylon 12,6 samples, with intrinsic viscosities ranging from 11 to 160 ml g^{-1} (m-cresol, 100°F) and melting points ranging respectively from 163° to 215°C. Furthermore, no compatibility of the latter samples with homogenized salt–water melts was obtained within the temperature range 120°–150°C, while the water content of the salt was varied between 30 and nearly zero mg H_2O/g of salt.

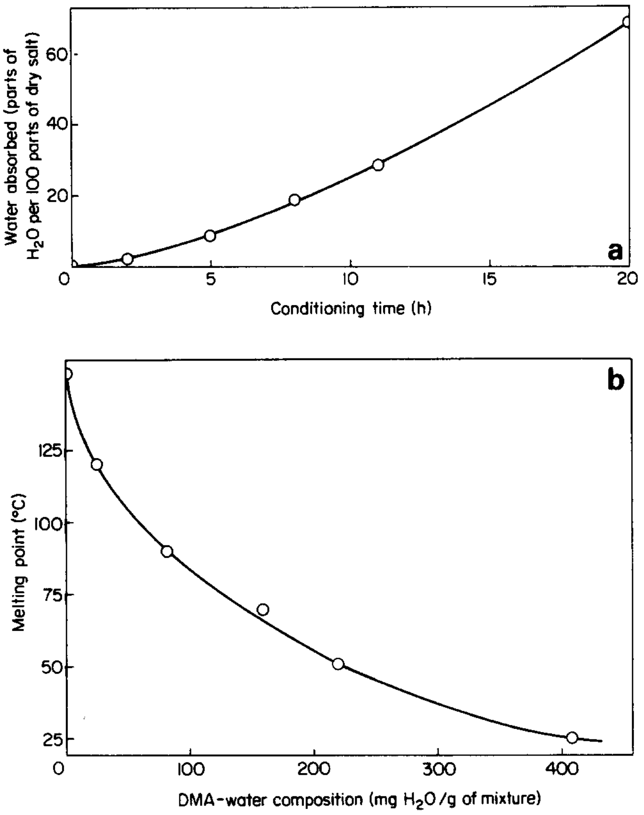

Figure 3 (a) Water absorbed by DMA salt *versus* conditioning time: (b) Influence of the moisture absorbed on the melting point of the DMA salt

Accumulation of water would be the result of the rate of water formation being faster than the rate of water removal. To investigate if this is the case, we have to calculate the difference between the quantity of the water formed and the water content of the reacting material. Accordingly, the quantity of water formed during SSP can be easily calculated by amine end-group determinations:

It is known that the conversion of p_t of the reaction is defined as the fraction of the functional groups that has reacted at reaction time t. Then

$$p_t=\frac{c_0-c_t}{c_0} \qquad (1)$$

where c_0, c_t represent concentrations at time $t=0$ and t respectively, usually expressed in gram equivalents per litre[19]. By assuming constant volume during the course of the reaction, equation (1) is transformed to the following:

$$p_t=\frac{(\text{g-equiv. of }-\text{NH}_2)_{t=0}-(\text{g-equiv. of }-\text{NH}_2)_t}{(\text{g-equiv. of }-\text{NH}_2)_{t=0}} \qquad (2)$$

or

$$p_t=\frac{(\text{moles of water produced})_t}{(\text{g-equiv. of }-\text{NH}_2)_{t=0}} \qquad (3)$$

Reducing for convenience our calculations per unit of reacting mass (g), equation (3) may be written:

$$m_{w,t} = 1.8 \times 10^4 \times p_t \times (\mathrm{N}_{-\mathrm{NH}_2})_{t=0} \tag{4}$$

where: $m_{w,t}$ = mass of polycondensation water produced up to reaction time t per unit of reacting mass, in mg g^{-1}; $(\mathrm{N}_{-\mathrm{NH}_2})_{t=0}$ = g-equiv. of amine end-groups per unit mass of the monomer salt.

The factor $(\mathrm{N}_{-\mathrm{NH}_2})_{t=0}$ could be also expressed as a function of the weight percentage of the amine end-groups contained in the monomer salt. Then equation (5) is obtained:

$$m_{w,t} = 11.25 \times p_t \times (c'_{-\mathrm{NH}_2})_{t=0} \tag{5}$$

where: $(c'_{-\mathrm{NH}_2})_{t=0}$ = weight percentage of amine end-groups in the monomer salt.

Let us suppose now that the reacting mass has a water content w_0 (mg g^{-1}) at time $t=0$ and w_t at time t. These values can be determined according to the Karl Fischer method. We define as 'Diffusion Parameter' D_t the following ratio:

$$D_t = \frac{w_t}{w_0 + 11.25 \times p_t \times (c'_{-\mathrm{NH}_2})_{t=0}} \tag{6}$$

D_t can be varied between 0 and 1. When there is no water accumulation in the reacting mass, i.e. when the water produced is quickly removed out of the grain, D_t tends to 0. In the opposite case, D_t tends to 1.

When applying the above analysis to the SSP of DMA very interesting results were obtained. In *Figure 4* the kinetic curves are shown for running the polymerization at 128°C, a typical intermediate temperature at which transition occurs. In *Figure 5* the curve A represents the quantity of the water formed while the curve B corresponds to the water content of the reacting mass. As can be seen, during the induction period[1] there is a surprising coincidence of the two curves. Alternatively the diffusion parameter D_t takes values little differing from unit (*Figure 6*). As the reaction enters the transition to the melt state, D_t decreases significantly and becomes minimum when the process is carried out in the melt state. Furthermore, microscopy studies on the samples taken did not lead to any indication of the formation of a water separate phase[5,9] while the heterogeneous character of the liquefied grains was again confirmed.

The above described experimental evidence confirming: (a) the fact that due to the moisture, the melting point of the DMA salt can be decreased well below the reaction temperatures employed; (b) the fact that a high percentage of the water formed is accumulated within the reacting material, and (c) the fact that the liquefied grains are heterogeneous, i.e. contain a dispersed solid phase, allows us to propose the following mechanism for the transition of the SSP of DMA to the melt phase:

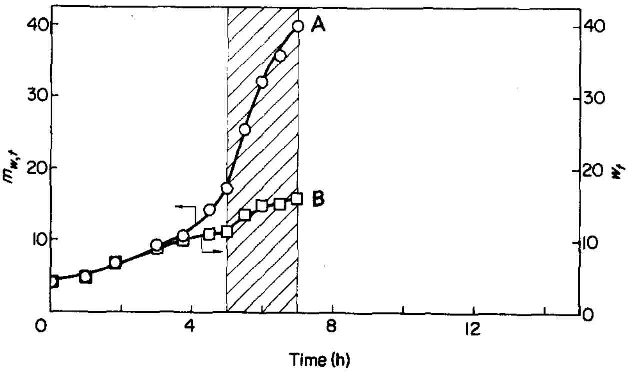

Figure 5 Plots of the polycondensation water formed $m_{w,t}$ (curve A) and of the water content of the reacting mass w_t (curve B) *versus* time

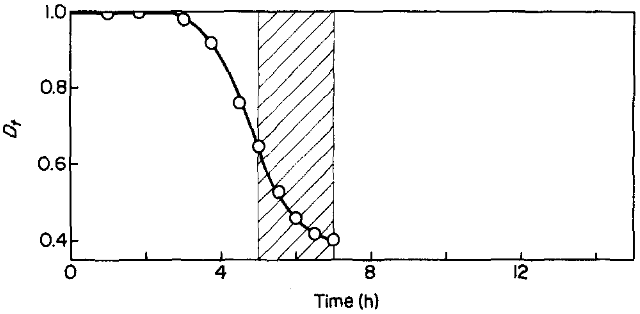

Figure 6 Diffusion parameter D_t *versus* time

The reaction begins at the defective sites of the monomer crystalline structure[20,21]. These defects constitute the active centres of the reacting solid, i.e. preferential reaction sites and in *Figure 7a* are given schematically for the inner part of a section of a typical salt grain. For active centres up to, or very near to, the grain surface the water formed can be easily removed to the surrounding liquid medium, without affecting the reacting mass. On the contrary, in the inner grain, the water cannot be easily removed and the points of water formation are surrounded with a 'highly hydrated' area of monomer. This 'highly hydrated' area has a lower melting point and, at the reaction temperatures studied, soon falls into the melt state. However, the polymer formed, being incompatible with the melt phase, eventually arises in the form of nuclei which are continuously increased according to a surface deposition process (*Figure 7b*).

After the formation of these melt areas, the reaction proceeds mainly in the melt state. As a result, the reaction rate is considerably increased, while the water accumulation leads to an increase of the total melt area (*Figure 7c*). Eventually an overlapping of these melt areas occurs (*Figure 7d*) which explains the observed transition of the reaction from the solid to the melt state. Of course, the melt obtained contains the polymer in dispersion.

According to the above proposed mechanism the DMA polycondensation could be considered to comprise three

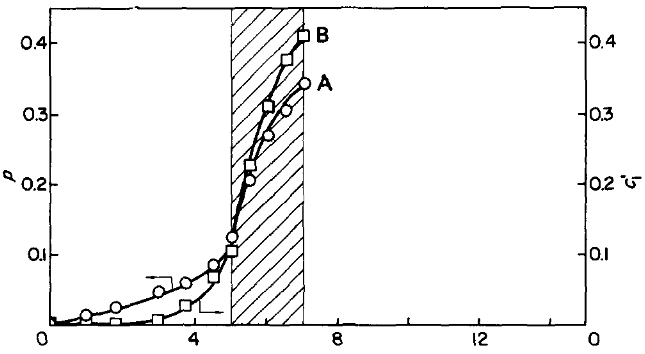

Figure 4 Plots of conversion p (curve A) and water-insoluble fraction c_i (curve B) *versus* time at 128°C[1]

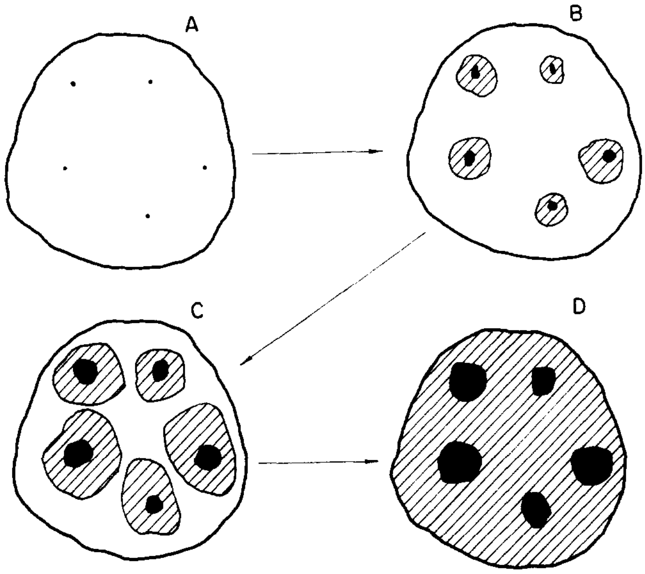

Figure 7 Solid state polyamidation of dodecamethylenediammonium adipate: A schematical explanation for the transition observed from the solid to the melt state. (·) = Defects of the monomer crystalline structure; Dark area = Polymer nuclei insoluble in water; Shaded area = 'Highly hydrated' and eventually melt area

stages:

(a) A pure solid state stage
(b) A 'quasi-solid' or, equally, 'quasi-melt' stage
(c) A melt stage

The induction period[1] may basically correspond to the pure solid state stage in which low reaction rates are in general encountered. However, the growth period observed, up to the transition point, corresponds to the quasi-solid or quasi-melt stage. During the course of this stage the reaction proceeds mainly in the continuously increasing melt areas, resulting in an increase in the reaction rate. Eventually, when overlapping of the melt areas occurs, the reaction falls totally into the melt stage and the reaction rate attains its maximum value.

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