

Solid state polyamidation of aliphatic diamine–aliphatic diacid salts: a generalized mechanism for the effect of polycondensation water on reaction behaviour

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Polycondensation reactions on nylon salts can be carried out in the melt or, alternatively, in the solid state. Nevertheless, in the latter case, a distinct transition to the melt state may take place, depending on the nature of the nylon salt and reaction temperature. For the particular case of the dodecamethylene–diammonium adipate this phenomenon has been attributed to water accumulation within the reacting structure. In this paper, based on previously reported preliminary results, the generalization of this mechanism is attempted for other typical cases of nylon salts, namely tetra- and hexamethylenediammonium adipate, and hexa- and dodecamethylenediammonium sebacate. All these salts when polymerized in the solid state may pass through a melt or quasi-melt stage. The polymerization runs were monitored both by end groups and water determinations. The experimental data obtained support the proposed mechanism according to which the polycondensation water tends to be sorbed at the polar hydrophilic groups with next effect the disturbance of the reacting regular structure. Then the mobility of the system increases and more water can be diffused out, but the reaction temperature plays a predominant role in the overall reaction behaviour.

(Keywords: nylon salts; solid-state polycondensation (polyamidation); solid–melt transition; water accumulation)

INTRODUCTION

Aliphatic diamine–aliphatic diacid polyamides are mainly synthesized through polycondensation of the corresponding nylon salts^{1,2}. The reaction can proceed either below or above the melting point of the starting material, i.e. the salt, and on an industrial scale synthesis the latter route is preferred. Nevertheless, this choice is accompanied by undesirable side reactions due to the comparatively higher reaction temperatures. Furthermore, diamines and diacids sensitive to these temperatures cannot be used³.

In previous papers from this laboratory^{4–10} the case of the solid state polyamidation (SSP) has been investigated for a considerable number of nylon salts. Initially, due to the stability of the dodecamethylenediamine against sublimation, the interest was focused on the dodecamethylenediammonium adipate used as a model salt⁴. In the absence of catalysts, the reaction rate was found to be drastically influenced by temperature. The more important finding, however, was that the temperature range to effect real solid state reaction is very limited. The reaction proceeds at a marked rate in a temperature range extending up to about 25°C below the melting point of the salt (151°C). However, even at the lower temperatures of this range, the reaction turns from the solid to the melt state.

A 'direct' solid state polyamidation, without an intermediate stage of reaction in the melt state, has not up to now been applied on an industrial scale. The observed solid–melt transition (SMT), clearly proved and discussed already^{4–8,10} seems to be a very good reason for that. Furthermore, in some relevant publications the pheno-

menon of the SMT is not obviously described, due to the experimental techniques followed^{11–20} (usually heating of some milligrams of the raw material in a closed chamber under inert atmosphere). A SSP reaction kinetics consistent with the appearance of the melt phase has been proposed, i.e. the kinetic data obtained very often fit well typical melt reaction models^{14,18}. In addition, considerable evidence exists for increased mobility of the reacting species^{18–22} and also for a distinct change of the reaction prevailing mechanism^{13,14,18,23}.

The importance of the role of the water formed during the course of polycondensation reactions has been thoroughly emphasized in the literature² a long time ago. On the contrary, what is surprising is that in many studies of the SSP reaction mechanism no role has been given to the water produced during the polycondensation process. Nevertheless in our laboratory, we detected considerable water accumulation by water quantitative determinations on the reacting material⁵. On the grounds of the deliquescent behaviour of the salt the formation of lower melting point areas was then proposed, overlapping eventually to effect a complete breakdown of the reacting crystalline structure. This behaviour has been assigned as mode II, to differentiate it from modes I and III, according to which no SMT takes place⁸. However, in the former case (mode I) diffusion of the water formed readily away from the reaction sites is supposed, while in mode III some of this water is accumulated in a second phase within the reacting structure. Accordingly, the generalization of these mechanisms was attempted by considering various nylon salts while varying the concentration and distribution of the amide forming groups¹⁰.

Table 1 Solid state polymerization runs: operational parameters

Grain size	600–700 microns
Ratio salt/inert solvent	20–25 g/l
Stirring rate	500 rpm
Distillation rate	150 ml/h
Dispersion agent	Wax montana (2% w/v)

The latter comprise typical hydrophilic sites, supposed to have significant interaction with the water molecules formed during the polymerization reaction^{10,24}. All the aliphatic diamine–aliphatic diacid nylon salts examined when subjected to SSP conditions, within reasonable reaction rates range, exhibited clearly the SMT phenomenon. It is the purpose of this paper to prove that this behaviour, in harmony with the results on dodecamethylenediammonium adipate, has to be attributed to water accumulation. Therefore, the SSP reactions are now monitored both by end-groups and water determinations.

EXPERIMENTAL

Preparation of nylon salts

The procedure already described for the preparation of the dodecamethylenediammonium adipate was followed⁴. Diamine and diacid were combined in exactly molecular proportions by bringing together ethanol (96%) solutions of equivalent amounts of the reactants. The white salt separated from the cooled solution may be used directly in the SSP process, comprising the monomer of the polymerization reaction.

Polymerization

The solid state polyamidation technique followed in this study has been described in detail previously⁴. In summary, the nylon salt was suspended in an inert solvent and the reaction was carried out, under stirring, at its boiling point, well below the melting point of the reacting solid. The method permits the use of significant quantities of nylon salt so that any SMT phenomena can be safely detected. When the solid state reaction turns to the melt state a very fast agglomeration of the reacting grains takes place, with the grains sticking to each other^{4,5,10}. The phenomenon can be readily seen macroscopically because stirring fails to keep the particles in suspension. Then if a sample is taken out of the reactor and examined in the microscope the transformation of the sharp-edged crystals to nearly spherical particles stuck together is clear. On the other hand, and independently of SMT, if water is forming a separate phase the reacting grains are then characterized by the presence of small bubbles¹⁰.

In *Table 1* the values of the operational parameters followed are quoted. Wax montana was used as a dispersion agent (2% w/v: 2 g of wax per 100 ml of non-solvent employed) to inhibit, as much as possible, any agglomeration of the reacting grains during 'quasi-solid' or equally 'quasi-melt stages' (QSMS) when softening starts. Obviously, this QSMS phenomenon is a precursor of the solid–melt transition⁵. Accordingly, by employing a suitable dispersion agent²⁶, one could possibly ensure continuous stirring so that the reacting grains are allowed to harden again⁴. This permits a more accurate study of the transition phenomena and microscopic observations are possible during the total

reaction course. It may be worthwhile to mention that montana wax comprises a typical mineral wax²⁷, supplied to us by Hoechst Hellas.

Characterization

Amine end-group analysis. Amine end-groups were determined according to the analytical procedure proposed by Waltz and Taylor²⁵. The results are easily correlated with the corresponding degree of conversion p assuming continuous equivalence of the reactive end-groups and absence of side reactions. This supposition was confirmed by parallel carboxyl groups determinations¹⁰.

Water quantitative determinations. The polycondensation water entrapped in the reacting grains was determined as follows. A sample was taken out of the reactor, washed with n-hexane and dried in an oven at 60°C for 10 min⁵. Subsequently the sample was dispersed in methanol and titrated with 'Karl Fischer' reagent²⁸. All results quoted in this study represent the average of three independent determinations.

Microscopic observations. An Amplival (Jenoptik Jena GmbH) microscope was employed at a magnification range between 50 and 200 ×.

RESULTS AND DISCUSSION

Selection of nylon salts

The aliphatic diamine–aliphatic diacid salts which were previously tested¹⁰ to give solid–melt transition phenomena, but without appearance of a separate water phase (mode II), include tetramethylenediammonium adipate; tetramethylenediammonium sebacate; hexamethylenediammonium adipate; hexamethylenediammonium sebacate; and dodecamethylenediammonium sebacate.

From the present study the case of the tetramethylenediammonium sebacate is excluded because we did not manage to prepare crystals from this particular salt within the magnitude range shown in *Table 1*. In fact, we aimed to use a rather narrow grain size because the latter may significantly influence the reaction rate¹⁶. Also, for microscopy observations this size should not be very small.

Selection of reaction temperature

As already mentioned any appearance of SMT phenomena is closely related with reaction temperature. In the extreme case of reaction temperatures much below the melting point of the nylon salt, SMT is excluded simply because the rate of the solid state polycondensation is very low⁴. For this reason, all salts were tested within a temperature range in which it is possible for SMT to occur, based on previous experimental findings¹⁰. Furthermore, in order to investigate the effect of the rate of the water formation, each salt was tested at two different reaction temperatures, one for moderate reaction rates and one for higher rates. In *Table 2* the temperature levels used for each particular salt are quoted together with the corresponding non-solvent used.

For each polymerization run curves of the following parameters are presented in agreement with previous investigations^{5,8}: conversion (p_i) vs. reaction time (t);

Table 2 Reaction temperatures selected

Nylon salt	Reaction temperature (°C)	Liquid employed
Tetramethylenediammonium adipate (m.p. 190°C)	151	n-Nonane
	174	n-Decane
	151	n-Nonane
Hexamethylenediammonium adipate (m.p. 192°C)	174	n-Decane
	138	p-Xylene
	151	n-Nonane
Hexamethylenediammonium sebacate (m.p. 171°C)	151	n-Nonane
	126	n-Octane
Dodecamethylenediammonium sebacate (m.p. 163°C)	138	p-Xylene

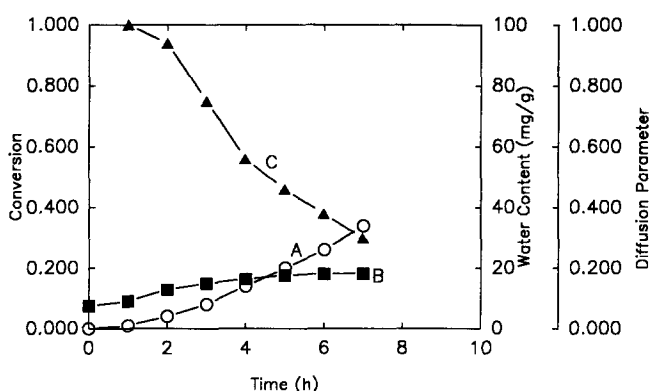


Figure 1 Tetramethylenediammonium adipate: plots of conversion p (curve A), of the water content of the reacting mass w_t (curve B) and of the diffusion parameter D_t (curve C) versus time at 151°C (b.p. of n-nonane): ○, p ; ■, w_t ; ▲, D_t

water content of the reacting mass (w_t) vs. t ; and diffusion parameter (D_t) vs. t .

The diffusion parameter has been defined in ref. 5 as the fraction of the water accumulated within the reacting grains over the sum of that initially present plus that formed during the polycondensation reaction. D_t can be varied between 0 and 1. When there is no water accumulation in the reacting mass, i.e. when the water formed is quickly removed out of the grain, D_t tends to 0. In the opposite case, it tends to 1. On the other hand, it should be mentioned that for all polymerization runs followed, independently of reaction rate, a separate water phase was not detected again by microscopic observations on the reacting crystals.

Moderate polycondensation rates

Tetramethylenediammonium adipate. In Figure 1 data for the system tetramethylenediammonium adipate/n-nonane are presented. The following observations can be made, all of which are consistent with the results from the SSP runs of the dodecamethylenediammonium adipate⁴.

The curve p_t vs. t (Figure 1, curve A) shows an induction period, lasting for 2 or 3 h. On the other hand,

by microscopic observations, after 2.5 h from the beginning of the reaction the appearance of a quasi-melt stage was evident. This phenomenon is of 1 h duration and then the reacting mass hardens again, i.e. the reaction returns to 'real' solid state conditions.

The total p_t vs. t data conform perfectly to the model of nucleation and growth⁴ because the correlation coefficient r^2 was found equal to unity.

From a water point of view, it is obvious that as time passes the water accumulated, w_t , increases and when the QSMS phenomenon appears it reaches its maximum value (Figure 1, curve B). This coincides nearly with the end of induction period. Afterwards, the reaction rate increases, but then more water can escape from the reacting grains. This behaviour can be alternatively seen by following the D_t vs. t curve (Figure 1, curve C). Initially, during the induction period, most of the water formed is accumulating within the reacting mass. This results in the appearance of the QSMS phenomenon according to the mechanism already proposed in ref. 5. The mobility of the system increases and then more water can be diffused away so that D_t decreases considerably. This trend does not change after the softening period and the reaction proceeds smoothly in the solid state.

Hexamethylenediammonium adipate. In Figure 2 the results of polymerizing hexamethylenediammonium adipate at the boiling point of n-nonane are presented. A very similar behaviour to that noted previously with tetramethylenediammonium adipate is encountered. The observations noted above are valid.

Hexamethylenediammonium sebacate. The behaviour of hexamethylenediammonium sebacate at moderate to low reaction rates is indicated in Figure 3. It differs significantly from the two previous salts in having a longer induction period (7 h). Again, microscopic observations provide evidence for the onset of a quasi-melt stage at the end of the induction period which results in some decrease of the diffusion parameter. Up to the end of the reaction time quoted (9.5 h) no hardening of the reacting grains was noticed. On the other hand, the correlation coefficient for the model of nucleation and growth is now equal to 0.96.

Dodecamethylenediammonium sebacate. In Figure 4 results are quoted for the case of the dodecamethylene-

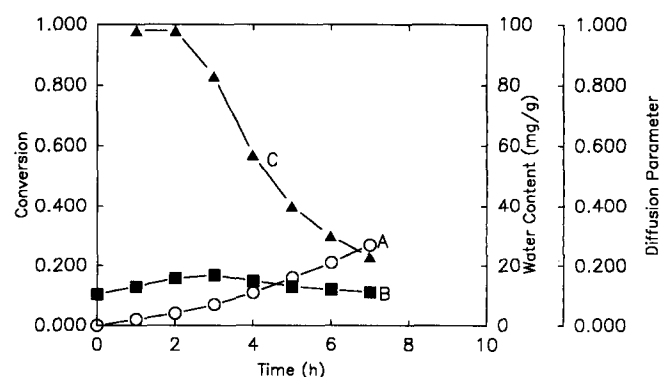


Figure 2 Hexamethylenediammonium adipate: plots of conversion p (curve A), of the water content of the reacting mass w_t (curve B) and of the diffusion parameter D_t (curve C) versus time at 151°C (b.p. of n-nonane): ○, p ; ■, w_t ; ▲, D_t

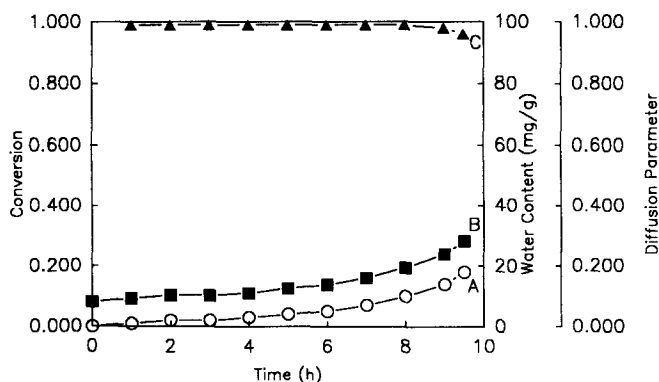


Figure 3 Hexamethylenediammonium sebacate: plots of conversion p (curve A), of the water content of the reacting mass w_t (curve B) and of the diffusion parameter D_t (curve C) versus time at 138°C (b.p. of *p*-xylene): ○, p ; ■, w_t ; ▲, D_t

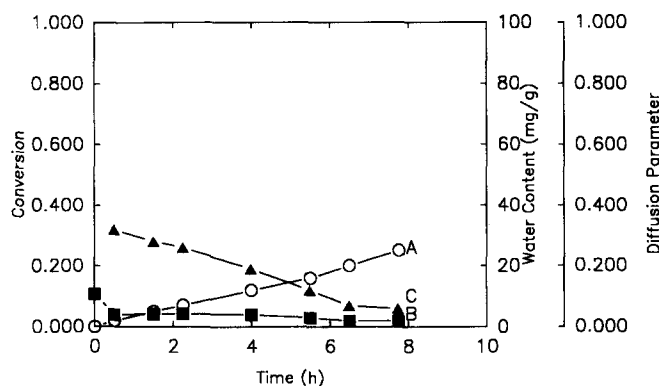


Figure 4 Dodecamethylenediammonium sebacate: plots of conversion p (curve A), of the water content of the reacting mass w_t (curve B) and of the diffusion parameter D_t (curve C) versus time at 126°C (b.p. of *n*-octane): ○, p ; ■, w_t ; ▲, D_t

diammonium sebacate. Significant deviations from the reaction pattern of Figures 1, 2 and 3 are encountered. Within our experimental conditions no QSMS phenomena were detected and consistently the water formed during the reaction seems to migrate easily out of the reacting grains (Figure 4, curves B and C). Furthermore, in the microphotographs of Figures 5 and 6 typical reacting particles can be seen at $t=0$ and $t=7.75$ h, respectively. Obviously, no transition to the melt state has occurred (as mentioned below), and only the sharp-edged crystals are smoothed out due to the continuous stirring applied.

High polycondensation rates

As previously discussed, when the reaction temperature increases, the effect on solid state polyamidation is very impressive, but the chances for the appearance of SMT phenomena are also multiplied, even in the presence of effective dispersion agents. The experimental results found for high polycondensation rates are discussed below.

Tetramethylenediammonium adipate. In Figure 7 the reaction behaviour can be seen at the boiling point of the *n*-decane, which is still 16°C below the melting point of the salt. In agreement with the behaviour of the dodecamethylenediammonium adipate under similar conditions⁴, the reaction from the very beginning is characterized by a distinct transition to the melt state

because the dispersion agent is not capable of inhibiting the agglomeration of the reacting grains. This melt stage lasts for 1.5 h and afterwards the reacting mass is solidified again so that the solid state character of the process is restored. On the other hand, during the initial melt stage and in spite of the high reaction rate, no considerable water accumulation is observed due to high mobility conditions in the reacting system⁵.



Figure 5 Typical crystals of dodecamethylenediammonium sebacate ($\times 100$)

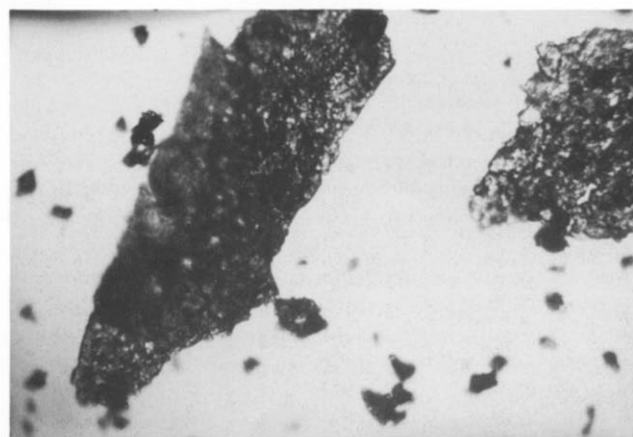


Figure 6 Reacted crystals of dodecamethylenediammonium sebacate after 7.75 h at 126°C ($\times 100$)

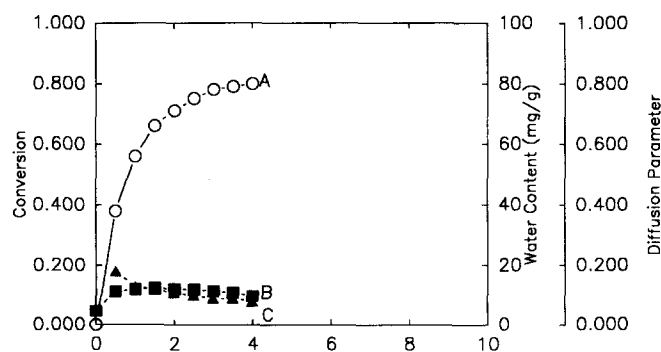


Figure 7 Tetramethylenediammonium adipate: plots of conversion p (curve A), of the water content of the reacting mass w_t (curve B) and of the diffusion parameter D_t (curve C) versus time at 174°C (b.p. of *n*-decane): ○, p ; ■, w_t ; ▲, D_t

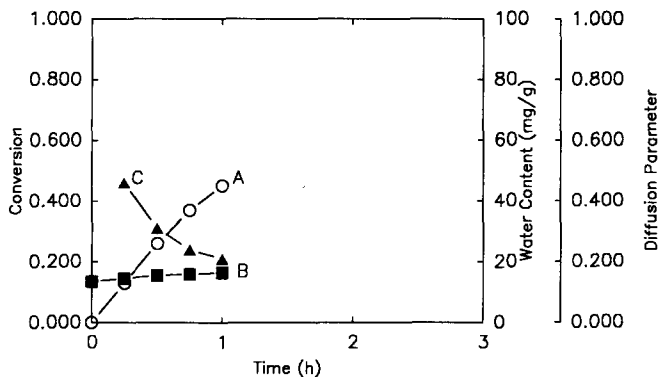


Figure 8 Hexamethylenediammonium adipate: plots of conversion p (curve A), of the water content of the reacting mass w_i (curve B) and of the diffusion parameter D_i (curve C) versus time at 174°C (b.p. of n-decane): \circ , p ; \blacksquare , w_i ; \blacktriangle , D_i

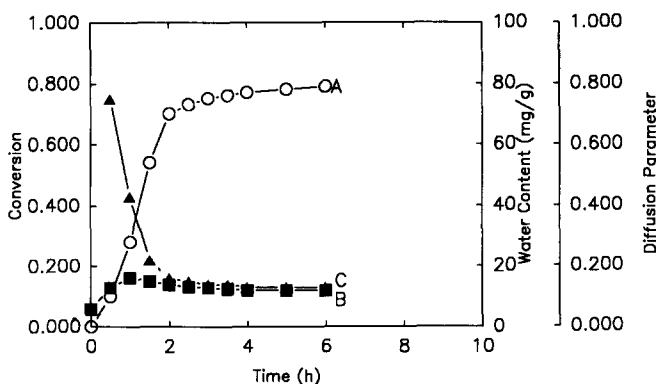


Figure 9 Hexamethylenediammonium sebacate: plots of conversion p (curve A), of the water content of the reacting mass w_i (curve B) and of the diffusion parameter D_i (curve C) versus time at 151°C (b.p. of n-nonane): \circ , p ; \blacksquare , w_i ; \blacktriangle , D_i

Hexamethylenediammonium adipate. As for the moderate reaction temperature, the hexamethylenediammonium adipate presents a very similar behaviour to the tetramethylenediammonium adipate. This becomes evident in Figure 8. Nevertheless, due to the fact that the melted grains are agglomerated to a very low viscosity unique mass, the continuation of the reaction beyond 1 h was not possible.

Hexamethylenediammonium sebacate. For the system hexamethylenediammonium sebacate/n-nonane the dispersion agent is proved to be quite effective and no SMT phenomena with extended grain agglomeration are observed, however readily evident without the dispersion agent¹⁰. Instead, from the very beginning a quasi-melt stage is observed which lasts for 1.5 h and ensures continuous removal of the considerable amounts of the water formed (Figure 9).

Dodecamethylenediammonium sebacate. The behaviour of dodecamethylenediammonium sebacate (Figure 10) resembles that of hexamethylenediammonium sebacate. Again, in spite of the higher reaction rates, only QSMS phenomena are observed from the very beginning. They last for about 3 h while the parameter D_i is restricted to low values. In Figure 11 a microphotograph of the reacting grains after 1 h of reaction can be seen. The quasi-melt stage is evident, especially in contrast to the microphotographs of the Figures 5 and 6.

Qualitative reaction model

The above mentioned observations may lead to the following qualitative model of reaction mechanisms.

It is a well known fact²⁹ that nylon salts from aliphatic diamines and aliphatic diacids provide different structural organization depending on their ability to crystallize in regular geometric patterns, in addition to the effect of intermolecular forces. Therefore, nylon salts formed from diamines and diacids of similar, but short, aliphatic length should be characterized by good structural organization due to the high concentration and uniform distribution of the polar hydrophilic groups. If this is the case, significant resistance to hydration should be attained. This assumption has already been proved¹⁰ and now, on the grounds of the above mentioned experimental results, we attempt to proceed further in understanding the effect of the polycondensation water as follows.

When the reaction rate is low, in the low range of reaction temperatures, a very high percentage of the water initially formed may be accumulated within the reacting structure, at the hydrophilic polar groups. This supposition is in complete agreement with the mechanism of water sorption in polyamides^{24,30}: primary hydration (firmly bound water), secondary hydration (loosely bound water) and 'cluster' water. The polar hydrophilic groups provide the first accommodating points and, of course, accessibility of moisture to the latter comprises

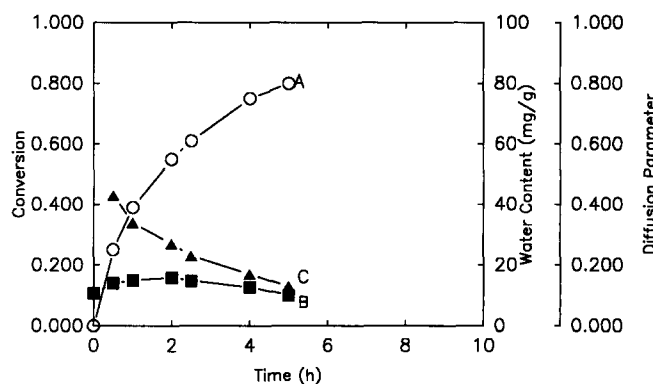


Figure 10 Dodecamethylenediammonium sebacate: plots of conversion p (curve A), of the water content of the reacting mass w_i (curve B) and of the diffusion parameter D_i (curve C) versus time at 138°C (b.p. of *p*-xylene): \circ , p ; \blacksquare , w_i ; \blacktriangle , D_i

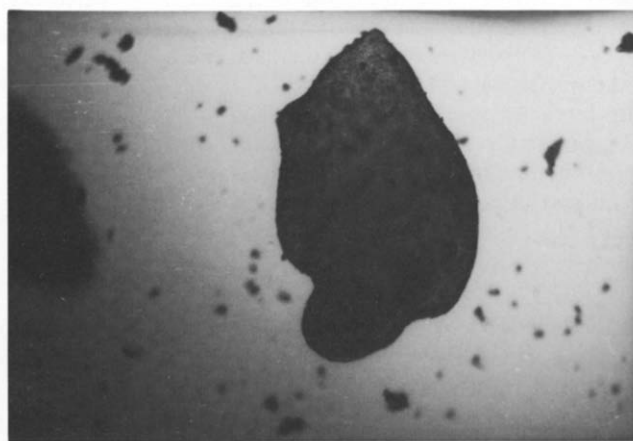


Figure 11 Reacted crystals of dodecamethylenediammonium sebacate after 1 h at 138°C ($\times 100$)

a very critical step. Similarly, in SSP polyamidations, it is expected that the first water molecules formed hydrate the polar groups of the salt structure. This is valid especially in the inner areas of the reacting crystals and their geometry becomes a quite important factor (e.g. Figure 5). Accordingly, the low reaction rate, i.e. low rate of water formation, ensures an organized accommodation of this by-product within the crystal structure. Progressively, the accumulated amount of water increases and then secondary hydration takes place so that the hygroscopic crystalline structure is loosened or disturbed by the formation of highly hydrated areas⁵. This corresponds to the end of the induction period and to the onset of a quasi-solid stage of increased mobility, accompanied by higher reaction rates and simultaneous decrease of the diffusion parameter D_i (Figures 1-4). In other words, diffusion away from the reacting sites of new water molecules formed is now more favoured. As the reaction proceeds further, the molecular weight increases, the hygroscopicity of the reacting system decreases⁵ and eventually the solid character of the process is restored.

The above picture may change drastically at high reaction rates, i.e. at higher reaction temperatures. The solid state polycondensation for the systems tetra- and hexamethylenediammonium adipate/n-nonane yields a distinct solid-melt transition even if the reaction temperature is still much below the melting point of the starting materials (Table 2). This can be explained simply by the fact that the time available for the stages of primary and secondary hydration, in a controlled manner, is very limited. In other words, due to the high rates of water formation, there is no time for an organized arrangement of the water molecules formed at the polar hydrophilic groups. As a result, the crystalline structure is very severely disturbed and depending on its nature¹⁰, is readily transformed to a highly hydrated area of increased mobility⁵ so that D_i is kept at low values. Afterwards, the system behaves similarly to the above mentioned QSMS phenomena.

The above mechanism seems quite valid for the case of nylon salts of a moderate structural organization. According to the terminology introduced in ref. 10, the salts examined present a typical 'mode II' behaviour, i.e. the reaction proceeds in the solid state and then (after some time or from the very beginning) turns to the melt or quasi-melt state. The appearance of any SMT or QSMS phenomena depend on the difference between the melting point of the salt and the reaction temperature while no water accumulation in a second phase within the reacting structure is detected. As already proposed in ref. 10, the latter finding seems to be a key point for the appearance of different solid state polyamidation modes, which have been correlated with the intrinsic characteristics of the starting material. For example, as an extreme case, the solid state polymerization of ethylenediammonium fumarate, even at very high reaction rates, does not proceed through SMT or QSMS phenomena.

Again this behaviour has been attributed to the possible interactions between the reacting structure and the polycondensation water formed¹⁰. In a later paper I will attempt a further investigation based similarly on continuously monitoring conversion, water content and crystal appearance during both solid state polymerization runs and for alternative reaction rates.

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