Solid-state polyamidation of nylon salts

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Solid-state polyamidation (SSP) processes may proceed through intermediates of lower melting point, resulting in a distinct solid–melt transition (SMT). In this study an attempt is made to correlate the phenomenon with structural characteristics of the starting material. Nylon salts formed from aliphatic diamines and aliphatic diacids were considered forst and, surprisingly, the same transitional behaviour was eventually detected independent of salt nature. However, when research was oriented to better organized salt structures, to effect increased resistance to hydration, the picture changed: ethylenediammonium fumarate provides no evidence for transition even at a reaction temperature closely approaching its decomposition point.

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

INTRODUCTION

Solid-state polyamidation (SSP) is of great interest in post-polymerizing nylon prepolymers produced in the melt state[1–7]. On the contrary, a direct SSP process, without intermediate stages of reaction in the melt state, has not up to now been applied on an industrial scale. Nevertheless, a considerable amount of research work has been accumulated on this alternative[1,8–16], as all the problems associated with the high temperatures of melt technology are absent.

In previous papers from our laboratory[17–20] the SSP of dodecamethylenediammonium adipate has been thoroughly examined. In the absence of catalysts[17,18], the reaction rate was found to be influenced drastically by temperature, but the range to effect true solid-state reaction appeared limited. In fact, even at temperatures significantly below the melting point of the crystalline salt, a transition of the process from the solid to the melt state was clearly observed. For an explanation of this phenomenon, the role of the water of polycondensation was considered. Water quantitative determinations proved that a significant amount of the water formed, during the course of the reaction, cannot be removed from the reacting grains. Consequently, on the grounds of the deliquescent behaviour of the salt, it was proposed that this water accumulation results in the formation of lower melting point areas, overlapping eventually to effect a complete breakdown of the reacting crystalline structure.

Solid–melt transition (SMT), during SSP processes, has rarely been referred to in the literature, either for nylon salts[10,21] or aminoacids[9], the typical monomer structures for these polymerization reactions. Nevertheless, the phenomenon is very compatible with the results of similar studies: considerable indications exist for increased mobility of the reacting species[4,5,15,16,22,23] and also for a distinct change of the reaction prevailing mechanism[11–13,15,16], while kinetic data obtained often fit well typical melt reaction models[16,22]. On the other hand, the appearance of lower melting point intermediates may be accompanied by separation of water formed in a second phase. This has been clearly pointed out by Kampouris[14] studying the SSP of hexamethylenediammonium maleate and also by Volokhina *et al.*[8] for ω-aminoheptanoic, ω-aminononanoic and ω-aminoundecanoic acids. Consequently, three different modes of SSP behaviour should be expected when starting directly from monomer:

Mode I. The reaction proceeds continuously in the solid state and the water produced readily diffuses away from the reaction sites.

Mode II. The reaction proceeds initially in the solid state and then, due to the formation of lower melting point intermediates, turns to the melt state. This mode corresponds to the dodecamethylenediammonium adipate behaviour.

Mode III. No transition to the melt state occurs, but some of the water produced is accumulated in a second phase within the reacting structure. The response of hexamethylenediammonium maleate seems to combine both modes II and III.

It is of great technological importance to be able to predict the appearance of mode II, as the control of the process, if this is the case, is completely lost[17]. In this paper the mechanism already proposed for dodecamethylenediammonium adipate[18] is further studied by correlating structural characteristics of the monomer with respective SSP behaviour. In particular, the case of nylon salts with the structural formula $\ldots H_3\overset{+}{N}(CH_2)_\chi\overset{+}{N}H_3{}^{-}OOC(CH_2)_\psi COO^{-}\ldots$ was first considered when varying χ and ψ, i.e. concentration and distribution of the amide-forming groups. The latter comprise typical hydrophilic sites[24,25], supposed to have significant interaction with the water molecules of the polymerization reaction.

EXPERIMENTAL

Preparation of nylon salts

All salts tested were precipitated from ethanol (96%) according to the general procedure already described for

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dodecamethylenediammonium adipate[17]. In particular, diamine and diacid are combined in exactly molecular proportions by bringing together ethanol solutions of equivalent amounts of the reactants. The white salt which separates from the cooled solution can be used directly in the SSP process, comprising the monomer of the polymerization reaction.

Polymerization

The SSP process, already described in detail[14,17], was followed throughout this study. The nylon salt was suspended in an inert non-solvent and the reaction was carried out, under stirring, at its boiling point, well below the melting point of the reacting solid.

Characterization

End-group analysis. $-NH_2$ and $-COOH$ contents were determined by titration according to the analytical procedure proposed by Waltz and Taylor[26]. The results are easily correlated with the corresponding degree of conversion, defined as the fraction of the reacted functional groups[18].

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

Solid–melt transition. As already mentioned[14,17–20], 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 one another. The phenomenon can be readily seen macroscopically since stirring fails to keep the particles in suspension. At this time, 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 numerous small bubbles[14].

RESULTS AND DISCUSSION

Selection of nylon salts

Linear polyamides prepared from aliphatic diamines and aliphatic diacids are characterized by amide group content, usually expressed in terms of the heterochain index[27]. The latter is defined as the ratio of the amide to the methylene groups in the polymer chain unit (molar percentages). Accordingly, the upper-left part of *Table 1* gives the aliphatic diamine–aliphatic diacid salts initially selected for study. The heterochain index of the respective polymers varies from 10.0 to 33.3%, ensuring a relatively wide range of hydrophilic site concentration within the reacting structure.

In *Table 1* experimental results from the stages of salt preparation and characterization are also given. (The case of the salts of ethylenediamine with either maleic or fumaric acid is included in *Table 1* and is discussed in detail later.) In general, good yields are negligible deviation from stoichiometric equivalence are confirmed. Therefore, no need arose for purifying the salts by recrystallization. However, to obtain a more uniform distribution of crystal size[16], the salts were recrystallized, under controlled conditions, from ethanol–water mixtures, and fractions between 150 and 250 μm were used throughout this study. No deviations from characterization data already quoted in *Table 1* were noticed because of the recrystallization process followed.

Solid-state polyamidation runs

According to the SSP technique applied and on the basis of the melting points determined for the salts prepared (*Table 1*), trying *p*-xylene (b.p. 138°C) first seemed worthwhile. Starting with the aliphatic diamine–aliphatic diacid salts, the results from this series of experiments, summarized in *Table 2*, proved very interesting. All salts of lower m.p. were characterized by distinct SMT. On the contrary, the SSP of the higher m.p. salts, i.e. tetramethylenediammonium adipate and hexamethylenediammonium adipate, appeared to proceed continuously in the solid state. This was also checked by microscopic observations of samples from the reacting crystals. For tetramethylenediammonium adipate 7 h of reaction resulted in a conversion of only 0.09 either on an amine or a carboxyl end-group basis, while hexamethylenediammonium adipate proved even more unreactive: after 20 h a conversion of 0.02 was not exceeded. Therefore, for the latter salts, the observed response might be attributed to the very low reaction rates attained, which are due to the great difference between the monomer m.p. and the reaction temperature employed[23].

To investigate further the relationship between reaction temperature and transition behaviour the SSP runs of hexamethylenediammonium sebacate, tetra-

Table 1 Nylon salts selected together with results on preparation yield, reactive end-group analysis and melting point determinations

Nylon salt	Polymer heterochain index (%)	Yield (%)	$-NH_{2,th}$ (%w/w)	$-NH_{2,d}$ (%w/w)	$-COOH_{th}$ (%w/w)	$-COOH_d$ (%w/w)	Melting point (°C)
Ethylenediammonium adipate	33.3	99	15.5	15.7	43.7	44.0	171
Ethylenediammonium sebacate	20.0	83	12.2	12.2	34.3	34.6	161
Tetramethylenediammonium adipate	25.0	90	13.7	13.8	38.4	38.7	190
Tetramethylenediammonium sebacate	16.7	92	11.0	11.3	31.0	31.3	175
Hexamethylenediammonium adipate	20.0	97	12.2	12.2	34.3	34.3	192
Hexamethylenediammonium sebacate	14.3	90	10.1	10.2	28.3	28.0	171
Dodecamethylenediammonium sebacate	10.0	91	8.0	8.0	22.4	22.7	163
Ethylenediammonium fumarate	–	97	18.2	18.3	51.1	51.3	161
Ethylenediammonium maleate	–	96	18.2	18.2	51.1	51.2	202[a]

[a] Decomposition point

th – Theoretical for stoichiometric equivalence

d – Determined

methylenediammonium adipate and hexamethylenediammonium adipate were repeated at temperatures closer to their melting point. As liquid medium the n-nonane (b.p. 151°C) was selected first and the results were indeed confirmatory. For hexamethylenediammonium sebacate, the time interval before SMT decreased from 2 h (at 138°C) to less than 5 min, a phenomenon similar to that noticed for dodecamethylenediammonium adipate (m.p. 151°C) reacting at 128 and 138°C[17]. For hexamethylenediammonium adipate the time interval before SMT was $2\frac{1}{6}$ h and the conversion then was 0.12. When the reaction was carried out at the boiling point of n-decane (174°C), rapid transition occurred for both salts, tetramethylenediammonium adipate and hexamethylenediammonium adipate.

Salt structure and SSP response

The experimental evidence quoted above makes it clear that mode II of the SSP response predominates for all the salts studied. On the other hand, combination with mode III has definitely been excluded, as no signs of water separation in a second phase were detected by microscopic observation. Accordingly, within the experimental limits, varying concentration and distribution of polar hydrophilic sites has no influence on SSP behaviour. In other words, if the mechanism proposed for dodecamethylenediammonium adipate[18] is accepted, the structure of the tested salts, under SSP conditions, remains vulnerable to the role of the water formed. Furthermore, no evident relationship arises between time interval before SMT and structural characteristics.

Rubin[28] pointed out, some time ago, 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, on the grounds of this statement, nylon salts formed from diamines and diacids of similar but short aliphatic length should be characterized by good structural organization. If this is the case, an increased melting point and significant resistance to hydration should be attained so that deviation from the transition mechanism could be effected.

In terms of the above consideration the study of the salt of ethylenediamine and fumaric acid seemed reasonable; its counterpart, the salt of ethylenediamine and maleic acid, was also included. The former should provide a highly organized structure, due to excessive polar content accompanied by the presence of the double bond in the more symmetric *trans* configuration. On the contrary, when changing the latter to the *cis* position a considerable decrease of structural order should be expected. These predictions are first confirmed by the m.p. determinations (*Table 1*), according to which the ethylenediammonium fumarate is characterized only by decomposition point.

Results from comparative polymerization runs are given in *Table 3*. Obviously, ethylenediammonium maleate exhibits a typical SMT behaviour even at a reaction temperature 23°C lower than its melting point. Nevertheless, in accordance with studies on hexamethylenediammonium maleate[14], the polyamidation reaction results also in evident separation of water formed in a second phase. This phenomenon, again on the grounds of the mechanism proposed for dodecamethylenediammonium adipate[18], is probably related to the increased resistance encountered by the water molecules when diffusing away from the reaction sites. Disorganized areas of the crystalline network may serve as accommodating points for the excess of water produced, and at high reaction rates, i.e. high water contents, complete breakdown does occur.

In contrast with the above behaviour, for the limiting case of ethylenediammonium fumarate, separation of water was again noticed, but all polymerization runs were continuously maintained in the solid state. Furthermore, the value of the conversion attained at 174°C, either on an amine or a carboxyl basis, should be emphasized, confirming the response of this particular salt according to SSP behaviour of mode III. In fact, with mode II, high

Table 2 Polymerization runs at the boiling point of *p*-xylene (138°C)

Nylon salt	Solid–melt transition (SMT) observed	Time interval before SMT (min)	Conversion at SMT
Ethylenediammonium adipate	+	50	0.07
Ethylenediammonium sebacate	+	40	0.07
Tetramethylenediammonium adipate	–	–	–
Tetramethylenediammonium sebacate	+	15	0.05
Hexamethylenediammonium adipate	–	–	–
Hexamethylenediammonium sebacate	+	120	0.10
Dodecamethylenediammonium sebacate	+	<5	–

Table 3 Comparative SSP runs of ethylenediammonium maleate and ethylenediammonium fumarate

	Nylon salt					
	Ethylenediammonium maleate			Ethylenediammonium fumarate		
Reaction temperature (°C)	110	126	138	138	174	195
Liquid medium employed	Toluene	n-Octane	*p*-Xylene	*p*-Xylene	n-Decane	n-Undecane
SMT observed	–	–	+	–	–	–
Time interval before SMT (h)	–	–	0.167	–	–	–
Total reaction time (h)	10	2	0.167	7	2	5
Conversion attained	0.11	0.15	0.05	0.03	0.55	–

reaction rates lead to a distinct transition to the melt, but this does not apply to the ethylenediammonium fumarate, even at 195°C, i.e. only 7°C below its decomposition point. Nevertheless, at this temperature and under our experimental conditions, oxidative actions became evident, decreasing the reliability of reactive end-group analysis.

Experimental evidence gathered up to now is clearly compatible with the significant role supposed for the water formed during SSP processes, so that correlation between monomer structural characteristics and SSP behaviour cannot be excluded. Nevertheless, it should be interesting to investigate model SSP runs of these salts by continuously monitoring conversion and water content accumulated within the reacting structure. Such investigations will be summarized in the near future.

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