Influence of acid catalysts on the solid-state polyamidation of dodecamethylenediammonium adipate

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Solid-state polyamidation is an alternative route for polyamide synthesis. Solid-state polyamidation of dodecamethylenediammonium adipate was studied in the presence of acid catalysts. Boric acid proved to be the most effective catalyst, followed by sulphuric acid, so that—even at high reaction rates—the reaction was maintained in the solid state throughout the process. On the other hand, phosphoric acid showed a clearly weaker action resulting eventually in a transition of the process from the solid to the melt state, in accordance with noncatalysed behaviour. In general, catalyst concentration plays a considerable role in the catalytic effectiveness obtained.

(Keywords: dodecamethylenediammonium adipate; solid-state polyamidation; acid catalysts; solid–melt transition)

INTRODUCTION

Solid-state polyamidation (SSP) is widely used in postpolymerizing nylon prepolymers produced in the melt phase[1–8]. Nevertheless, solid state polyamidation, without any intermediate stages of reaction in the melt phase, has until now not been used industrially. Such a process would ensure total avoidance of undesirable side reactions and make feasible the utilization of diamines and diacids that are sensitive to high temperatures. Accordingly, a considerable amount of research work has been accumulated on such 'pure' solid state processes[1,9–20]. However, the disadvantages that have been detected include low rates of the polycondensation reaction[9,19] and transition of the reaction from the solid to the melt phase[9,15,17–20]. In the latter instance, there is rapid agglomeration of reacting particles whereby control of the process is completely lost. A possible mechanism for this transition has been proposed recently[20]. To overcome the problem various catalysts have been proposed[2,5,6,9,12–14]. These increase the polyamidation rate and also should favour maintenance of the process in the solid state.

In catalytic solid-state polyamidation homogeneous distribution of the catalyst is difficult. Up to now either mechanical mixing of monomer particles with a solid catalyst[2,12–14] or impregnation of prepolymer in a catalyst solution[5,6] have been proposed. Nevertheless, it remains questionable whether these incorporation processes ensure a homogeneous catalytic activity throughout the mass of reacting particles.

Solid-state polyamidation of dodecamethylenediammonium adipate (DMA) has been studied in the absence of catalysts[19,20]. This particular salt was chosen as a model system because of its low melting point and stability with respect to sublimation of dodecamethylenediamine. Consequently this choice ensured a strict control of the polymerization, monitored mainly by decrease of the amine content. Reaction rate was found to be strongly influenced by temperature; nevertheless at high reaction rates the characteristic solid–melt transition was clearly observed.

In this paper results are presented of studies on the SSP of DMA in the presence of the catalysts boric acid, sulphuric acid and phosphoric acid. A new technique of catalyst incorporation was used, the results of which are very satisfactory: reaction rate is considerably increased while the transition to the melt state is no longer encountered.

EXPERIMENTAL

Preparation of the catalyst-containing nylon salts

Catalyst incorporation in the monomer was based on an unpublished coprecipitation technique due to the authors according to which the catalyst is coprecipitated simultaneously with the nylon salt. Thus, 25.1 g (0.125 mol) of dodecamethyelenediamine was dissolved in 125 ml of ethanol (96 vol%) with warming (40°C), and then the solution was cooled to room temperature. In addition, 18.3 g (0.125 mol) of adipic acid together with catalyst was dissolved in 125 ml of ethanol. The quantity of the catalyst added was varied in order to study the catalytic effectiveness over a range of catalyst concentrations. The acid solution was added quantitatively to the stirred diamine solution, while cooling, to maintain the temperature below 30°C. Stirring was continued for 1 h, after the addition of all the acid solution, and the reaction mixture was cooled to 0°C and left overnight to assist deposition of the salt formed. The separated product was filtered, washed with cold ethanol and dried in a circulating air oven (4 h; 40°C) and subsequently under vacuum over P_2O_5 (24 h; 20°C).

In *Table 1* the catalyst content expected and determined, as well as the yield of the corresponding

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Table 1 Preparation of nylon salts: yield and catalyst content

Catalyst	Catalyst content Expected (wt%)	 Determined (wt%)	Yield (%)
Sulphuric acid	1.00	1.16	86.4
	2.00	2.08	83.9
	6.00	5.93	45.2
	16.00	15.72	29.8
Phosphoric acid	1.00	0.74	95.5
	2.00	2.06	94.0
	3.00	3.27	89.6
	7.00	6.92	85.2
Boric acid	0.50	0.46	90.8
	0.70	0.69	92.2
	1.00	0.92	91.4
	2.00	2.29	73.1

precipitation process, are given for each salt prepared. As can be seen, the presence of the compounds added, under the experimental conditions followed, seems to interfere considerably in the salt precipitation process, especially for sulphuric acid. On the other hand, excellent dispersion of the added catalyst was detected by repeated analytical determinations. Catalyst content analysis was based on SO_4^{2-}, PO_4^{3-} and elemental boron determinations: SO_4^{2-} and PO_4^{3-} were determined gravimetrically[21], whereas boron was determined by inductively coupled plasma atomic emission spectrometry (spectral line, 249.67 nm). Analytical data expressed as SO_4^{2-}, PO_4^{3-} and B contents are transformed, for convenience, to H_2SO_4, H_3PO_4 and H_3BO_3 contents respectively.

All the salts prepared were studied by infra-red spectroscopy. The spectra show great similarity to the spectrum of pure DMA[19]. The presence of a zwitterion form is again evident, i.e. the structure

$$H_3\overset{+}{N}(CH_2)_{12}\overset{+}{N}H_3 \;\vdots\; {}^{-}OOC(CH_2)_4COO^{-}$$

predominates. On the other hand, X-ray analysis resulted in the same crystallographic peaks encountered in the diffractogram of the pure DMA salt[19]. Furthermore, no differences in solubility characteristics were detected. In particular, all the catalyst-containing monomers were readily soluble in water.

Polymerization

The SSP process proposed by Kampouris[15] was followed throughout this study. The starting material was suspended in an inert solvent and the reaction was carried out at the boiling point of the solvent. The particle size of the salt, the ratio of salt to inert solvent and the distillation rate were kept at the levels of −400 mesh (US Sieve Series), 40–60 g l^{-1} and 150 ml h^{-1}, respectively. The reaction was followed by monitoring the amine end groups and the water-insoluble fraction[19]. The final products were also characterized by viscosity measurements[22], i.r. spectroscopy and X-ray diffraction analysis.

RESULTS AND DISCUSSION

Effect of catalyst content on SSP

In a previous study[19] it was found that at the boiling point of n-octane (126°C) the DMA polyamidation rate, in the absence of catalysts, was very low. Just 2 K above this temperature the reaction rate is much greater but also, after some time, the reactants have become completely molten. Therefore, it seemed worthwhile to run the catalytic polyamidations at 126°C, as reference temperature.

Figures 1a, *2a* and *3a* present, for each catalyst tested, isochronous curves of conversions *versus* the catalyst content of the monomer. The conversion was calculated on the basis of reduction of amine end groups. *Figures 1b*, *2b* and 3b show similar curves that present the variation of the water-insoluble fraction *versus* catalyst content. The superiority of boric acid is evident. Compared with the other acid compounds, significantly higher degrees of conversion are obtained with lower catalyst contents. Phosphoric acid shows no marked catalytic activity.

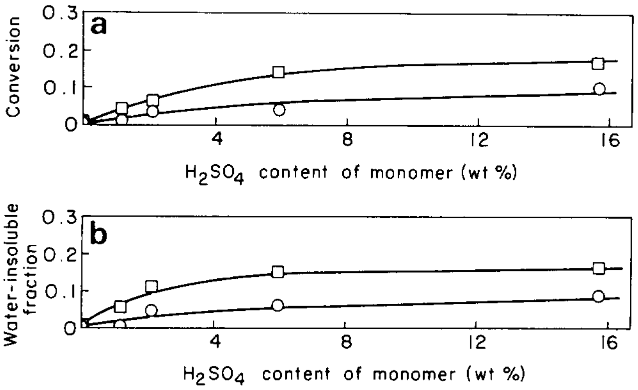

Figure 1 Plots of conversion (a) and water-insoluble fraction (b) vs. H_2SO_4 content of monomer for various reaction times: (○) 4 h; (□) 8 h

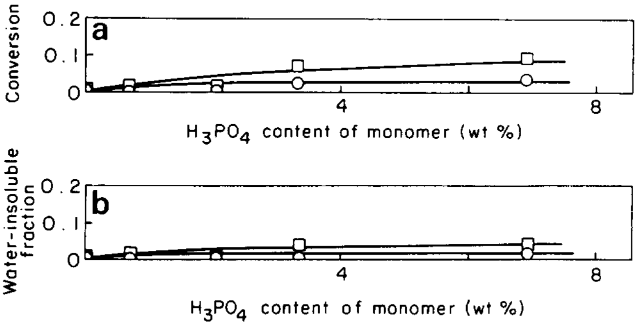

Figure 2 Plots of conversion (a) and water-insoluble fraction (b) vs. H_3PO_4 content of monomer for various reaction times: (○) 4 h; (□) 8 h

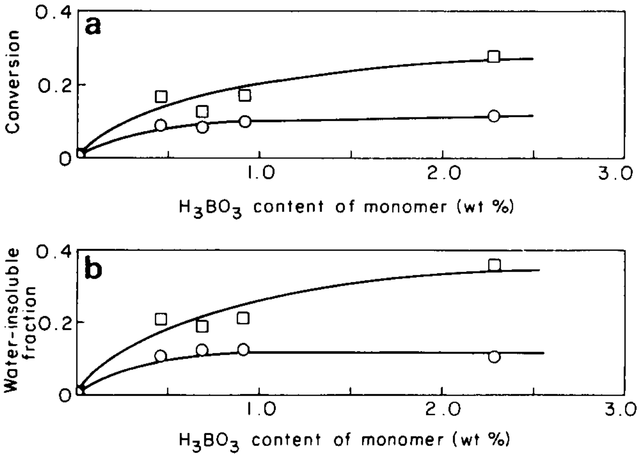

Figure 3 Plots of conversion (a) and water-insoluble fraction (b) vs. H_3BO_3 content of monomer for various reaction times: (○) 4 h; (□) 8 h

Nevertheless, independently of the nature of the catalyst the extent of the reaction seems to increase parabolically with catalyst concentration.

Effect of reaction time on the catalytic SSP process

Figures 4, *5* and *6* (first 24 h only) present kinetic curves of the reaction carried out at 126°C in the presence of the acid compounds tested. The catalyst-containing monomers used are of a moderate catalyst content within the ranges studied. For comparison similar non-catalytic curves, at the same temperature, are shown in *Figure 7*[19]. In all cases, the existence of a nucleation period followed by a period of growth is evident. For boric and sulphuric acid the duration of the nucleation period is about 14 h, whereas for the phosphoric acid it seems to extend up to about 18 h. The following order of catalytic effectiveness is again observed: $H_3BO_3 > H_2SO_4 > H_3PO_4$.

This order of effectiveness becomes more evident by continuing the reaction at higher temperatures (*Figures 4–6*). From 24 h to 36 h the reaction temperature was gradually increased from 126 to 138°C ($1\ K\ h^{-1}$) by feeding the reactor with *p*-xylene instead of n-octane. The reaction rate, as a function of either reduction of amine end groups or increase of the water-soluble fraction, increased considerably and eventually decreased smoothly. At the end conversions and yields respectively equal to 0.80 and 0.96 for boric acid and 0.60 and 0.96 for sulphuric acid were obtained. However, for the 'weak' phosphoric acid typical non-catalytic behaviour was observed: just 2 h after the temperature elevation a rapid transition to the melt state occurred.

The products of the successful catalytic processes were further characterized by viscometry, i.r. spectroscopy and X-ray diffraction analysis. The limiting viscosity numbers determined were found equal to 35 and $16\ ml\ g^{-1}$ (m-cresol, 100°F) for boric and sulphuric acid respectively. Obviously, boric acid favours a faster increase of formed polymer chains. On the other hand, i.r. spectra as well as X-ray diffractograms were similar to those obtained from products of noncatalytic SSP. A typical polyamide structure was confirmed together with the characteristic crystallographic peaks of nylon 12,6 at 3.7, 4.4 and 19.9 Å[19].

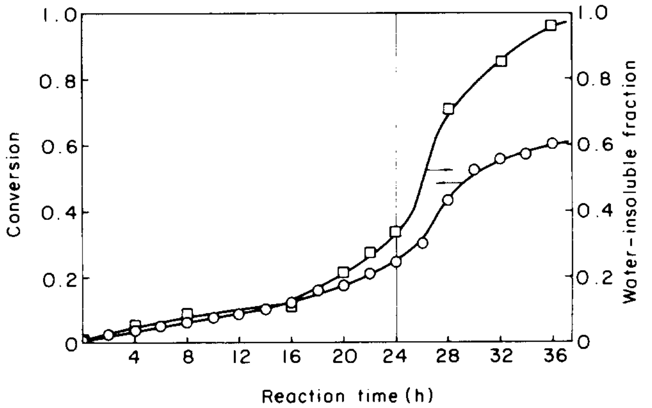

Figure 4 Catalytic SSP of DMA containing 2.08 wt% H_2SO_4: (○) conversion; (□) water-insoluble fraction. Up to 24 h the reaction proceeds at 126°C, from 24–36 h the temperature is increased by $1\ K\ h^{-1}$

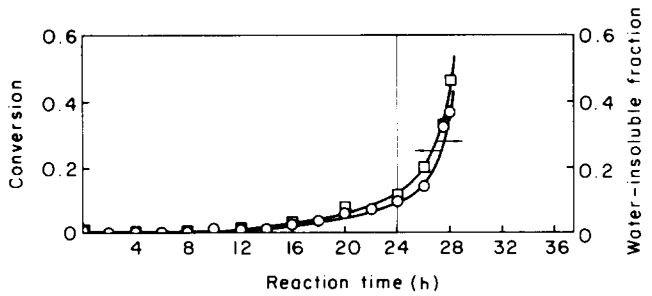

Figure 5 Catalytic SSP of DMA containing 2.06 wt% H_3PO_4: (○) conversion; (□) water-insoluble fraction. Temperature programmed as in *Figure 4*

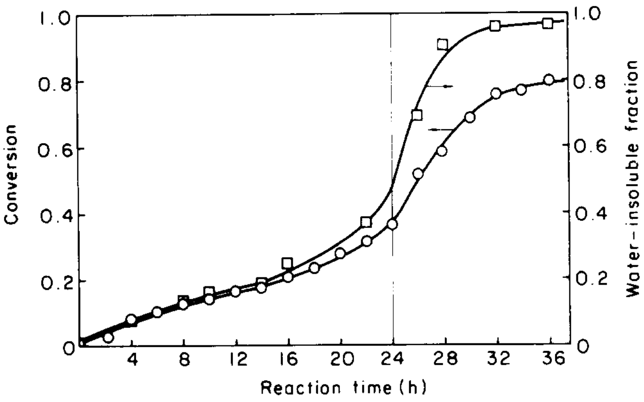

Figure 6 Catalytic SSP of DMA containing 0.46 wt% H_3BO_3: (○) conversion; (□) water-insoluble fraction. Temperature programmed as in *Figure 4*

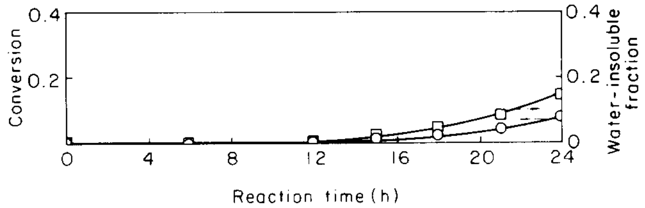

Figure 7 Solid state polymerization run of DMA at 126°C in the absence of catalysts[19]: (○) conversion; (□) water-insoluble fraction

In all cases no removal of catalyst was noticed during the polyamidation process. Catalyst content of the reaction products was determined and no difference from that initially present was detected.

CONCLUSIONS

1. It is feasible to prepare nylon 12,6 of considerable molecular weight by solid state polymerization of DMA in the presence of acid catalysts. No intermediate stages of melt reaction are included. The process proposed comprises a polymerization run carried out first at 126°C and then at regularly increasing temperature up to 138°C.
2. Under the experimental conditions, boric acid proved to be the most effective catalyst for the DMA solid-state polycondensation, followed by sulphuric acid. Phosphoric acid showed weak catalytic behaviour that with acceleration of the reaction rate was also accompanied by a rapid transition of the process to the melt state.
3. In general, catalytic behaviour increases parabolically with catalyst content. No catalyst separation was detected during the polyamidation process owing to the coprecipitation procedure followed for catalyst incorporation in the monomer particles.

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