Influence of metal catalysts on solid state polyamidation of nylon salts

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Oxides, hydroxides or salts of various metals of Groups IIA, VA and VIII of the periodic table were tested as catalysts for the solid-state polyamidation of dodecamethylenediammonium adipate, chosen as a model nylon salt. The metal compounds were incorporated by coprecipitation or nucleation. Comparative polymerization runs showed that dibasic sodium arsenate heptahydrate (DSAH) was the most effective catalyst so that it was studied in detail: DSAH-containing monomers, prepared by coprecipitation, showed a more consistent behaviour while arsenic concentration seemed to influence the catalytic activity up to a limiting value of about 0.1 wt%.

(Keywords: dodecamethylenediammonium adipate; solid-state polyamidation; metal catalysts; nucleation; coprecipitation)

INTRODUCTION

Solid state polyamidation (SSP) reactions of nylon salts or prepolymers avoid high temperatures and undesirable side reactions and/or decomposition of the raw materials. Previous papers have dealt with solid state polymerization of dodecamethylenediammonium adipate (DMA) in the absence[1,2] or presence[3] of catalysts. DMA was selected as a model nylon salt because of stability with respect to sublimation of dodecamethylenediamine, which ensures accurate study of the reaction kinetics[4,5]. Catalysts studied up to now comprise typical acid compounds, such as boric acid, sulphuric acid and phosphoric acid; the following relative order of catalytic effectiveness was established: $H_3BO_3 > H_2SO_4 > H_3PO_4$ (ref. 3).

In general, metal catalysts are encountered in SSP processes. Volokhina *et al.*[5] in a study of the SSP of various hexamethylenediamine-based nylon salts proposed the following order of catalytic effectiveness: 1% H_3BO_3, 0.2% $MgO > 0.5\%$ $(COONH_4)_2 > 0.5\%$ $(CH_3COO)_2Zn > 0.2\%$ $Na_2CO_3 > 0.6\%$ $CH_3COOH > 0.5\%$ $(NH_4)_2SO_4 > 1\%$ $SnCl_2$. Similar work on the SSP of hexamethylenediammonium adipate by Khripkov *et al.*[6] resulted in the following series: $H_3BO_3 > (CO_2H)_2 > H_3PO_4 > MgO$; Na_2CO_3, $NaHSO_4$ and $(SiO_2)_n$ proved totally inactive. Bruck in a paper concerned with solid state polyoxamidation catalysts[7] proposed the following compounds listed according to their effectiveness: $SbF_3 \sim As_2O_3 \gg GeO_2 > Sb_2O_3 > Bi_2O_3 \sim PbO$.

Literature information on catalyst incorporation is limited to either mechanical mixing of the solid catalyst with the starting material (either monomer or prepolymer)[7-10] or impregnation in a catalyst solution[11,12]. Nevertheless, in the authors' laboratory a new incorporation technique has been developed in which the metal compound acts either as a nucleating agent during the monomer precipitation or it is coprecipitated together with the nylon salt[13].

The non-catalytic SSP of DMA, run at 126°C, proceeds at a very low rate[1,2]. When the temperature is increased by only 2°C the reaction rate markedly increases, but also a transition of the process to the melt state eventually takes place. In this research the catalytic activity of various metal compounds was studied with regard to obtaining considerable acceleration of the reaction rate but also maintenance of the reacting particles in the solid state. Such behaviour is related to catalyst nature, catalyst concentration, reaction temperature and reaction time.

EXPERIMENTAL

Preparation of the catalyst-containing nylon salts

Metal compounds, such as oxides, hydroxides and salts, were tested as catalysts. *Table 1* lists all the compounds used, classified according to the groups of the periodic table.

To prepare the metal-containing nylon salts, i.e. the starting materials of the catalytic polymerizations, alternative procedures were followed depending on the solubility of the particular metal compound in the diacid (or diamine) solution employed[1]. If soluble, the experimental procedure described previously[2] was followed and the catalyst was coprecipitated together with the nylon salt. Otherwise, the 'nucleation' procedure, referred to above, was applied: the metal compound was dispersed in the diacid (or diamine) solution and then the diamine (or diacid) solution was added to under stirring. Catalyst micronized particles act as a nucleating agent in the subsequent precipitation process.

Catalyst content determinations in the salts prepared were based on metal quantitative analysis by atomic absorption spectrometry (a.a.s). On the other hand arsenic determinations were further confirmed by X-ray fluorescence analysis (XRF)[13] because of the reduced reliability of the a.a.s. data relating to arsenic. In general, satisfactory dispersion of the catalysts added was confirmed by repeated analytical determinations, especially for the salts prepared by coprecipitation.

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Table 1 Metal compounds tested as catalysts for the solid state polyamidation of dodecamethylenediammonium adipate

Group		
IIA	VA	VIII
$Ca(OH)_2$	As_2O_3	Fe_2O_3
$Sr(OH)_2 \cdot H_2O$	Na_3AsO_3	Co_2O_3
$Ba(OH)_2 \cdot 8H_2O$	$Na_2HAsO_4 \cdot 7H_2O$	Ni_2O_3
	Sb_2O_3	$NiSO_4 \cdot 6H_2O$
	Bi_2O_3	

Table 2 Precipitation yield and catalyst content of various salts prepared by 'nucleation', together with conversion after reacting for 8 h at 126°C

Metal compound	Catalyst content (wt%)	Yield (%)	Conversion
$Ca(OH)_2$	0.62	88.5	0.07
$Sr(OH)_2 \cdot H_2O$	0.38	96.2	0.01
$Ba(OH)_2 \cdot 8H_2O$	1.00	94.4	0.05
As_2O_3	0.65	93.9	0.11
Na_3AsO_3	1.03	96.4	0.28
$Na_2HAsO_4 \cdot 7H_2O$	1.12	93.6	0.50
Sb_2O_3	1.07	96.1	0.06
Bi_2O_3	0.93	95.2	0.05
Fe_3O_3	1.60	97.9	0.04
Co_2O_3	1.60	96.5	0.07
Ni_2O_3	0.90	98.3	0.00
$NiSO_4 \cdot 6H_2O$	0.82	99.1	0.09
No catalyst	0.00	96.0	0.00

Infra-red spectroscopy studies of all the prepared salts showed a zwitterion form. The spectra and X-ray diffractograms were similar to those of pure DMA[1]. Differences in solubility characteristics between pure and catalyst-containing DMA were slight.

Polymerization

A solid state polymerization technique[14] was used. The reaction was followed by monitoring the amine end groups and the water-insoluble fraction[1]. Final products were further characterized by viscometry, i.r. spectroscopy and X-ray diffraction analysis.

RESULTS AND DISCUSSION

Effect of catalyst on DMA solid state polyamidation

To study the effect of catalyst nature, salts containing the metal compounds under investigation were prepared by nucleation. *Table 2* lists for each salt the catalyst content determined together with the yield of the corresponding precipitation process. Clearly, the presence of the incorporated metal compounds, under the experimental procedure followed, does not seem adversely to affect precipitation yield.

The catalytic effectiveness of the metal compounds was evaluated under stnadard reaction conditions[1,3]: temperature, 126°C (boiling point of n-octane) and time, 8 h. The results, based on amine end group analysis, are quoted in *Table 2*. Clearly, DSAH has the greatest catalytic effectiveness among the metal compounds tested while, within each group of the periodic table, the following order is established:

Group IIA $Ca(OH)_2 \geqslant Ba(OH)_2 \cdot 8H_2O > Sr(OH)_2 \cdot H_2O$
Group VA $Na_2HAsO_4 \cdot 7H_2O > Na_3AsO_3 > As_2O_3 > Sb_2O_3 \geqslant Bi_2O_3$
Group VIII $NiSO_4 \cdot 6H_2O \geqslant Co_2O_3 \geqslant Fe_2O_3 > Ni_2O_3$

These series reveal the important role not only of the nature of the metal element itself, but also of the nature of the chemical compound employed, either oxide, hydroxide or salt. In fact, DSAH or nickel sulphate hexahydrate are clearly superior to arsenic(III) oxide or nickel(III) oxide respectively.

Effect of DSAH concentration on DMA solid state polyamidation

Because of its effectiveness DSAH was studied in more detail. First of all it seemed worthwhile to relate catalytic effectiveness to catalyst content. Accordingly, DMA containing different amounts of catalyst was prepared. Two ranges of catalyst concentration were examined: salts that contained 0.23–2.06 wt% elementary arsenic (high) were prepared by nucleation while those that contained 0.03–0.18 wt% (low) were prepared by coprecipitation. *Table 3* lists determined arsenic content and precipitation yield. The presence of DSAH, in various concentrations, does not interfere in salt precipitation.

All salts were polymerized in the solid state at 126°C and the resulting amine content decrease and water-insoluble fraction increase were determined. *Figures 1* and *2* present isochronous curves of conversion and water-insoluble fraction *versus* catalyst concentration. Low consistency of catalytic behaviour is evident for salts of high arsenic content, which is explained in terms of catalyst distribution. On the other hand, consistent results are obtained for coprecipitating catalyst together with salt. Furthermore, at these relatively low catalyst concentrations the resulting differences in catalytic effectiveness are negligible. The latter seems to be influenced by catalyst content up to a value of about 0.1 wt% arsenic.

Effect of reaction time on the DSAH-catalysed SSP of DMA

Figures 3 and *4a* present typical kinetic curves of DMA solid state polyamidation carried out at 126°C in the presence of moderate amounts of DSAH. Compared with similar non-catalytic curves[1,3] the acceleration of the process is evident, independently of incorporation procedure.

In a previous study[3] we found that when DMA polyamidation (run under identical conditions) is acid-catalysed kinetic curves revealing nucleation and growth periods are obtained. Such behaviour is not encountered with DSAH; further, for long reaction times (up to 24 h), a drop in the catalytic effectiveness is observed instead (*Figure 4*). Nevertheless, the catalyst is very effective in

Table 3 Precipitation yield and arsenic content in DSAH-containing salts prepared by nucleation or coprecipitation

Nucleation		Coprecipitation	
Arsenic content (wt%)	Yield (wt%)	Arsenic content (wt%)	Yield (wt%)
0.23	95.7	0.03	96.3
0.49	97.1	0.09	93.6
0.97	92.1	0.09	93.7
1.12	93.6	0.15	90.4
1.18	96.2	0.18	94.1
1.21	95.6		
1.71	93.3		
2.06	94.5		

maintaining the overall process in the solid state. Even for higher reaction rates, by increasing the reaction temperature from 126 to 138°C over 12 h (1 K h^{-1})[3], no transition to the melt state occurred (*Figure 4b*).

The product of the latter run was further characterized by viscometry, i.r. spectroscopy and X-ray diffraction analysis. A limiting viscosity number equal to 28 ml g^{-1} (m-cresol, 100°F) was determined while i.r. spectra and X-ray diffractograms were similar to those obtained from products of noncatalysed SSP. Accordingly, 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[1].

No problems of catalyst removal were encountered during the polymerization runs, which the authors found to be usual in the case of simply mixing the catalyst with the monomer employed. Therefore the observed drop in the catalytic effectiveness during the long polymerization run of *Figure 4* cannot be correlated with any catalyst separation. In fact, the catalyst content remained constant and equal to 0.09 wt% throughout the process.

CONCLUSIONS

1. Some metal compounds have a clear catalytic effect on DMA solid state polyamidation. The nature of the metal element itself, and the nature of the chemical compound employed are of considerable importance.
2. Among the metal compounds tested dibasic sodium arsenate heptahydrate proved to be the most effective catalyst, independently of incorporation procedure. Nevertheless, salts rich in catalyst and prepared by nucleation failed to provide a reliable catalytic behaviour.

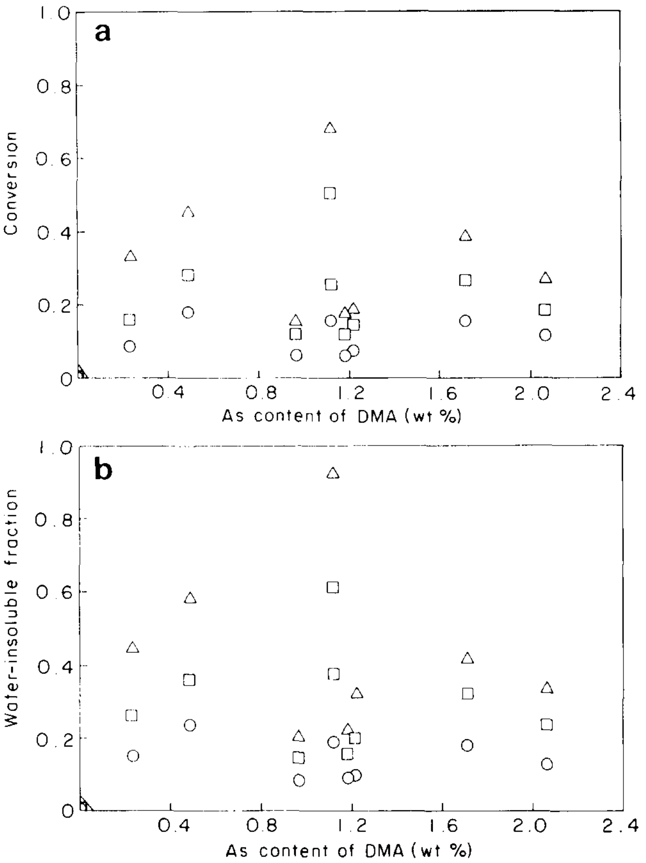

Figure 1 DSAH-containing salts prepared by nucleation. Relation between conversion (a) or water-insoluble fraction (b) and catalyst content for various reaction times (h) at 126°C: (○), 4; (□), 8; (△) 12

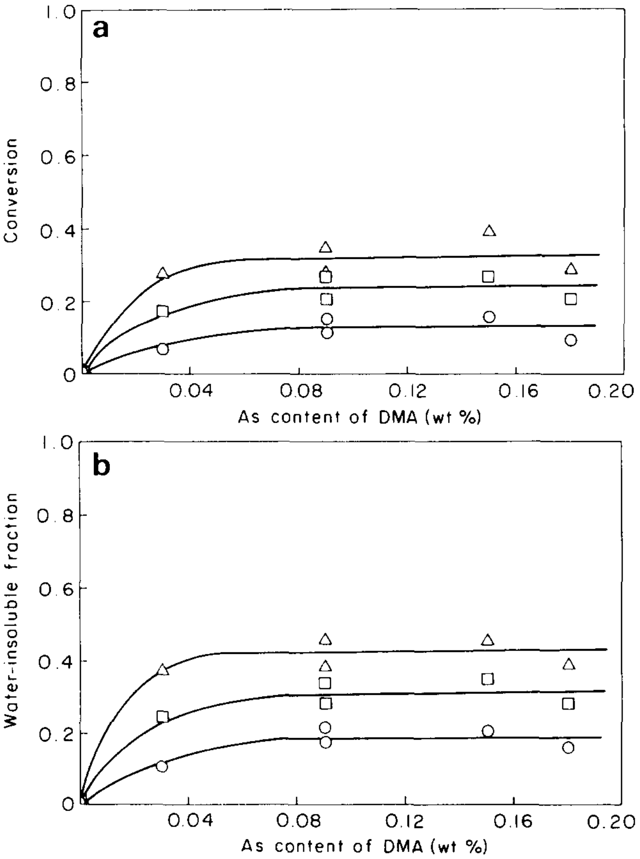

Figure 2 DSAH-containing salts prepared by coprecipitation. Relation between conversion (a) or water-insoluble fraction (b) and catalyst content for various reaction times (h) at 126°C: (○), 4; (□), 8; (△), 12

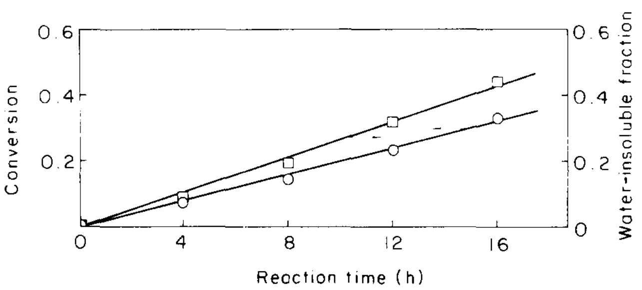

Figure 3 DSAH-containing salts prepared by nucleation. Typical kinetic curve of solid state polymerization runs carried out at 126°C (As content of DMA, 1.21 wt%): (○) conversion; (□) water-insoluble fraction

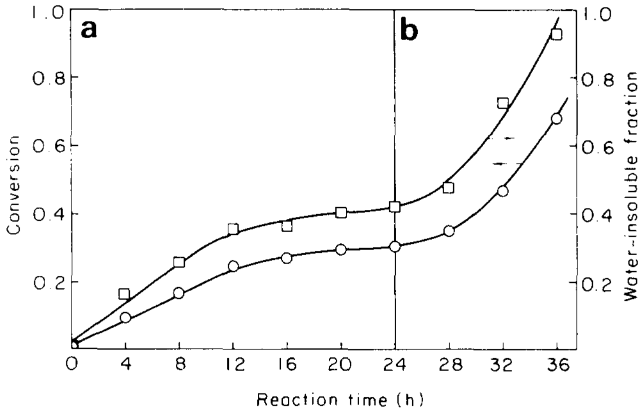

Figure 4 DSAH-containing salts prepared by coprecipitation. Typical kinetic curve of solid state polymerization runs (As content of DMA, 0.09 wt%). Reaction temperature kept at 126°C for 24 h (a), then increased by 1 K h^{-1} (b). (○) conversion; (□) water-insoluble fraction

On the contrary, the salts of low arsenic content prepared by coprecipitation gave more reliable results that indicated a parabolic increase of the catalytic activity with catalyst concentration.

3. Nylon 12,6, in a good yield, can be obtained by solid-state polymerization of DSAH-containing dodecamethylenediammonium adipate. The reaction temperature must be kept at 126°C and after some time raised gradually to 138°C. No problems of catalyst separation were encountered in spite of the solvent polymerization technique.

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