Solid-state polyamidation of dodecamethylenediammonium adipate

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The solid-state polyamidation of nylon salts comprises an attractive research field. The low sublimation rate of dodecamethylenediamine ensures salt stability and accurate relationships between amine end-group analysis and extent of the reaction. This accuracy is further enhanced by studying the solid-state polyamidation of dodecamethylenediammonium adipate (DMA), a nylon salt with a low melting point. Reaction rate was found to be influenced drastically by temperature, but the temperature range to effect true solid-state reaction is actually limited. Even at temperatures significantly below the melting point of DMA, a transition of the process, from the solid to the melt state, was clearly observed. Kinetic data obtained were tested against well known solid-state and melt reaction models. Nevertheless, none of them can exclusively describe the polyamidation studied, possibly because the true reaction model should take into consideration the process leading to the solid–melt transition observed.

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

INTRODUCTION

Melt polyamidations are the most common in the case of polyamides prepared from diamines and diacids. Nevertheless, the high temperatures of melt reactions accelerate undesirable side reactions, and diamines and diacids sensitive to these temperatures cannot be used. In contrast, solid-state polyamidations proceed at considerably lower temperatures and therefore comprise an attractive process that alternatively may be applied. In fact it has been proposed, even for applications on an industrial scale, first to polymerize the nylon salts in the melt state and then to complete the reaction by postpolymerization in the solid state[1,2].

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. However, it attracts the interest of many polymer technologists, as all the problems associated with the high-temperature disadvantages of melt technology are absent. In addition the polymer product is obtained in finely divided form ready for feeding to the usual equipment of polyamide processing[3].

In an attempt to describe the kinetics and to establish the actual reaction mechanism for solid-state polyamidation of nylon salts or prepolymers, various models have been proposed. Such models, common in solid-state reactions, include the model of nucleation and growth[4–10], the model of diffusion- or phase-boundary-controlled reaction[5,11] and the first-order[6], second-order[10,12] or linear kinetics models[7,8,10]. In addition, Griskey and Lee[13] proposed a power-law model, common in decomposition reactions. Furthermore, Chen, Griskey and Beyer[14] assumed Fickian diffusion of the

polycondensation water in the solid polymer and proceeded to derive appropriate rate functions from experimental data.

It is well known that the differences between many of these models are not very significant, i.e. in many cases the data obtained from different equations agree well within experimental error. Usually, kinetic data are based on amine end-group analysis or weight loss due to the water produced. The possibility of amine separation[15] or even water accumulation within the reacting mass[16] decreases the accuracy of the latter method greatly. Amine end-group analysis primarily requires increased stability of diamine against sublimation, throughout the polymerization process. Therefore, in an attempt to investigate the actual reaction mechanism of the solid-state polycondensation of nylon salts, dodecamethylenediammonium adipate (DMA) was chosen. It is known that dodecamethylenediamine is very stable against sublimation, in contrast to aliphatic diamines of shorter length, such as hexamethylenediamine[15,17]. In addition, DMA has a low melting point and therefore lower reaction temperatures can be utilized, leading to even greater stability of diamine. This situation would not be possible by increasing the length of the aliphatic diacid[18,19].

In this paper are presented the results of studying the effect of time, temperature and presence of dispersion agents on the solid-state polymerization of DMA. Reaction rate was found to be influenced drastically by temperature, and at high reaction rates a very interesting transition was noticed: the reaction medium changes from the solid to the melt state, even at temperatures significantly below the melting point of the salt. An attempt to describe the kinetics of the reaction has also been included by testing the kinetic data obtained against well known reaction models.

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EXPERIMENTAL

Preparation of dodecamethylenediammonium adipate

A solution of adipic acid (73.1 g; 0.50 mol) in 500 ml of ethanol (96%) was added slowly to a stirred solution of dodecamethylenediamine (100.2 g; 0.50 mol) in 500 ml of ethanol (96%) while cooling to maintain the temperature at 30°C. Stirring was continued for 1 h after the addition of all the adipic acid, and the reaction mixture was cooled at 0°C to assist deposition of the salt formed. The separated product was filtered, washed with cold ethanol (96%) and dried, first in a circulating air oven (4 h; 40°C) and subsequently under vacuum over P_2O_5 (24 h; 20°C) to give 166.5 g (96%) of dodecamethylenediammonium adipate.

Polymerization

In this study the solid-state polyamidation technique proposed by Kampouris[20] was followed. The non-solvents used include: (a) n-octane, (b) p-xylene and (c) mixtures of n-octane and p-xylene. The polymerization reaction was followed by monitoring the amine end-group content and the water-insoluble fraction. To secure isothermal conditions across the reacting grains, the grain size of the salt was kept at the level of minus 400 mesh (US Sieve Series). The ratio salt/inert solvent and the distillation rate were kept at the levels of 40–60 g l^{-1} and 150 ml h^{-1} respectively.

To correlate intrinsic viscosity data with molecular weight, model oligomers were prepared in the melt state. The melt reactions were carried out in an autoclave at 200°C for 2 h: 20 g of starting material was charged into a polymer tube placed in the autoclave, which was purged of air by alternately evacuating and flushing with nitrogen. After 60 min heating at atmospheric pressure, the product was gradually brought to high vacuum and heating was continued for another 60 min.

Characterization

The characterization of the salt was based on elemental analysis, amine end-group analysis, melting point determination, i.r. spectroscopy and X-ray diffraction analysis.

The characterization of the reaction products was based on amine end-group analysis, determination of the water-insoluble fraction, viscosity measurements, cryoscopy measurements, i.r. spectroscopy and X-ray analysis.

Amine end-group analysis. Amine end-groups were determined according to the analytical procedure proposed by Waltz and Taylor[21]. 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.

Determination of the water-insoluble fraction. To determine the water-insoluble fraction (c_i), about 2 g of sample, accurately weighed (± 0.001 g), were stirred with 80 ml of water for 10 min, left overnight, transferred to a fritted glass filter (medium size), washed with water, vacuum-dried, and weighed.

Viscosity measurements. The viscosity of the polymerization products was measured, with an Ostwald viscometer, on solutions in m-cresol at 100°F. The intrinsic viscosity (η) was determined according to the procedure described in ASTM D2857-70.

Cryoscopy measurements. The cryoscopic method in phenol was used for the determination of the molecular weight of the model oligomers prepared. It is a well known procedure[22] for polyamides of molecular weight of up to 5000.

Infra-red spectroscopy. A Perkin–Elmer 267 infra-red spectrophotometer was used. All the samples were investigated in a nujol mud.

X-ray diffraction analysis. All X-ray diffractograms were taken with the use of nickel-filtered copper radiation ($\lambda = 1.5418$ Å).

Kinetic calculations

Owing to the stability of dodecamethylenediamine, the establishment of a kinetic model was based on amine end-group analysis. In kinetic studies, postulations of the mechanisms of reactions are based primarily on the best fit of plots of p (the fraction reacted) vs t (the time of reaction) with plots of equations derived on the basis of various models. Such model processes, already referred to in the literature, are quoted in *Table 1* together with the corresponding mathematical expressions $f(p)$ or $f(\bar{M}_n)$. In this study our data were tested against one equation after another: $f(p)$ (or ln $f(\bar{M}_n)$) was plotted against t (or ln t) using the technique of linear regression. Linearity, revealing the best fitting model process, was evaluated primarily by the coefficient of determination r^2.

Table 1 Model processes

Type of reaction	Mathematical expression	
Diffusion-controlled		
One-dimensional	p^2	$= kt$
Two-dimensional	$(1-p)\ln(1-p)+p$	$= kt$
Three-dimensional	$[1-(1-p)^{1/3}]^2$	$= kt$
	$(1-2p/3)-(1-p)^{2/3}$	$= kt$
Phase-boundary-controlled		
Circular disc or cylinder reacting inwardly	$1-(1-p)^{1/2}$	$= kt$
Sphere reacting inwardly	$1-(1-p)^{1/3}$	$= kt$
Nucleation and growth	$[-\ln(1-p)]^{1/2}$	$= kt$
	$[-\ln(1-p)]^{1/3}$	$= kt$
Power-law model (Griskey and Lee)	$\ln(\bar{M}_{n,t}-\bar{M}_{n,0}) = \ln[k/(n+1)]$ $+ (n+1)\ln t$	
Chen, Griskey and Beyer diffusional model	$\ln K(t) = \ln k' + m \ln t$ where	

$$\bar{M}_{n,0}/\bar{M}_{n,t} = \frac{8}{\pi^2}\sum_{n=0}^{\infty}\frac{1}{(2n+1)^2}e^{-(2n+1)^2K_1(t)}$$

or

$$\bar{M}_{n,0}/\bar{M}_{n,t} = \frac{6}{\pi^2}\sum_{n=1}^{\infty}\frac{1}{n^2}e^{-n^2K_2(t)}$$

Kinetics models		
Linear kinetics	p	$= kt$
First-order kinetics	$-\ln(1-p)$	$= kt$
Second-order kinetics	$1/(1-p)-1$	$= kt$
Third-order kinetics	$1/(1-p)^2-1$	$= kt$

RESULTS AND DISCUSSION

Characterization of the nylon salt

Dodecamethylenediammonium adipate melts at 151°–152°C, is soluble in water (pH of 1% solution, 7.3), is slightly soluble in the lower alcohols, and is insoluble in paraffinic, aromatic and chlorinated hydrocarbons. Quantitative elemental and amine end-group analysis gave: C, 62.5; H, 11.3; N, 8.2; and $-NH_2$, 9.3%. $C_{18}H_{38}O_4N_2$ requires: C, 62.3; H, 11.0; N, 8.1; and $-NH_2$, 9.2%.

The infra-red spectrum of the salt reveals a zwitterion form of the following type:

$$... H_3\overset{+}{N}(CH_2)_{12}\overset{+}{N}H_3\overset{-}{O}OC(CH_2)_4C\overset{-}{O}O ...$$
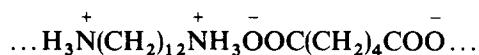
Thus, $-COOH$ absorption at $1700\,cm^{-1}$ is missing. There is strong absorption at $2200\,cm^{-1}$ due to the presence of $\overset{+}{N}H_3$; absorption at $1660\,cm^{-1}$ corresponding to asymmetric bending of $\overset{+}{N}H_3$; absorption at $1570\,cm^{-1}$ corresponding to asymmetric stretching of $CO\overset{-}{O}$; absorption at $1515\,cm^{-1}$ corresponding to symmetric bending of $\overset{+}{N}H_3$; absorption at $1410\,cm^{-1}$ due to symmetric stretching of $CO\overset{-}{O}$; and absorption at $1125\,cm^{-1}$ due to transverse rolling vibration of $\overset{+}{N}H_3$.[6,23]

The X-ray diffractogram of the salt is typical of a crystalline solid. Four strong reflections can be distinguished corresponding to 3.9, 4.1, 4.4 and 5.0 Å. There appear also some other weaker reflections at 20.1, 3.7, 6.8 and 3.3 Å.

Effect of temperature on the polymerization process

Temperature is known to influence significantly the rate of solid-state polyamidations, especially in a temperature range lying close to the melting point of the salt[15,17]. Accordingly, it is common to run the polymerization just a few degrees below the monomer melting point[12,15,24,25]. It is questionable, however, whether such a process indeed takes place in the solid state or in a quasi-solid state[16,20]. In fact, in the case of DMA, we found that true solid-state polymerization is not feasible near the melting point of the salt. Even at 138°C (13°C below the DMA m.p.) the reaction medium changes from the solid to the melt state in a few minutes. Subsequently the temperature effect on DMA polyamidation was examined in the range of 99° to 138°C. Within this range, great differences in the polymerization rate were noticed.

Polymerization of the salt for 24 h at the boiling points of iso-octane (99°C) and toluene (111°C) did not result in any significant conversion. Nevertheless, as the distance from the DMA m.p. becomes smaller, the effect of temperature becomes more pronounced: at the boiling point of n-octane (126°C) the reaction proceeds considerably faster. In this case, after reaction for 24 h, the degree of conversion and the water-insoluble fraction reached values of 7.7 and 14.1% respectively (*Figure 1*). Consequently, the polycondensation of dodecamethylenediammonium adipate proceeds at a marked rate starting with temperatures approximately 25°C below its melting point. Such a situation has also been observed for the case of hexamethylenediammonium adipate[15].

According to *Figure 1*, the existence of an induction period, lasting for about 16 h, is evident. The curve based on amine end-group analysis is quite similar to that
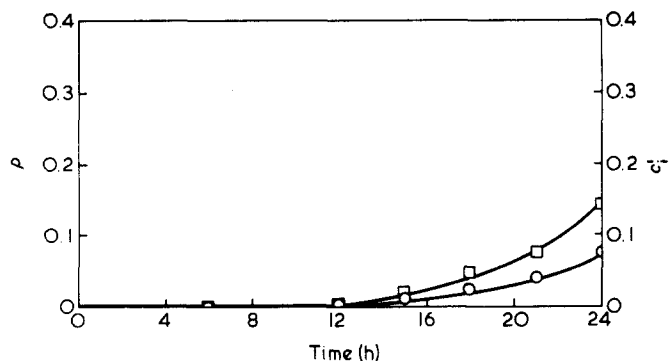

Figure 1 Plots of conversion p (O) and water-insoluble fraction c_i' (□) vs reaction time at 126°C
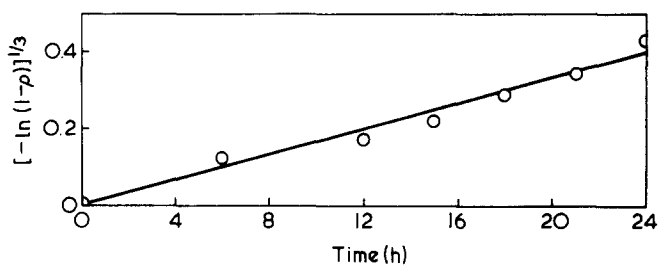

Figure 2 Relationship between $[-\ln(1-p)]^{1/3}$ (model of nucleation and growth) vs time at 126°C

corresponding to the water-insoluble fraction determinations. On the other hand, only the nucleation and growth model was found to fit the experimental data well ($r^2 = 0.97$). This good agreement is clearly shown in *Figure 2*. The correlation coefficients for the other models tested are as follows: diffusion models, 0.46; phase-boundary-controlled models, 0.70; Griskey and Lee model, 0.93; linear kinetics, 0.69; first-order kinetics, 0.69; second-order kinetics, 0.68; and third-order kinetics, 0.67.

At the boiling point of p-xylene (138°C) the rate of polymerization is increased tremendously. Nevertheless, within some minutes, a transition to the melt state is easily noticed, as all the grains become sticky and eventually agglomerate. This state continues until formation of a product of higher melting point and then the reaction proceeds again in the solid state, but at a very much lower rate. The effect of time on conversion and water-insoluble fraction is given in *Figure 3* in which the melt stage is indicated by the shaded area.

By testing the data of the polymerization run at 138°C against the model processes of *Table 1*, it was found that after solidification of the reacting mass the diffusion-controlled models, either one-, two- or three-dimensional, fit the corresponding experimental data well ($r^2 = 0.99$). The latter were fitted equally well by the models proposed by Griskey and Lee ($r^2 = 0.99$) or by Chen, Griskey and Beyer ($r^2 = 0.99$). In contrast, the following r^2 values were found for the other models tested: phase-boundary-controlled, 0.92; nucleation and growth, 0.75 and 0.66 (exponent n equal to 2 or 3 respectively); linear kinetics, 0.90; first-order kinetics, 0.92; second-order kinetics, 0.94; and third-order kinetics, 0.95. On the other hand, during the melt stage the reaction was found to proceed according to second-order kinetics ($r^2 = 0.98$), common for melt polyamidation[26,27]. *Figure 4* shows clearly the good agreement with the second-order and diffusion-controlled models prevailing during the two stages of the reaction, melt and solid respectively.
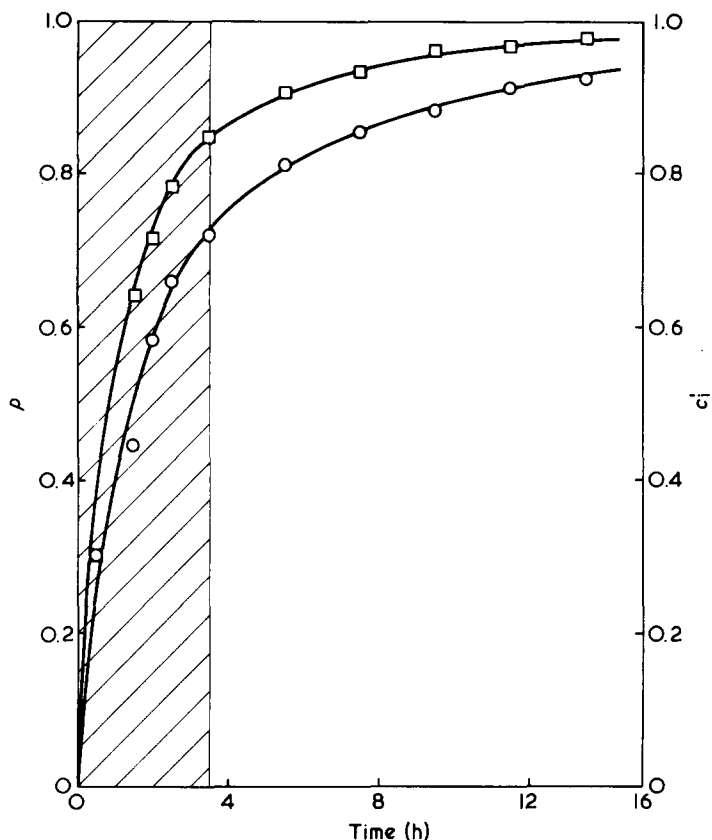
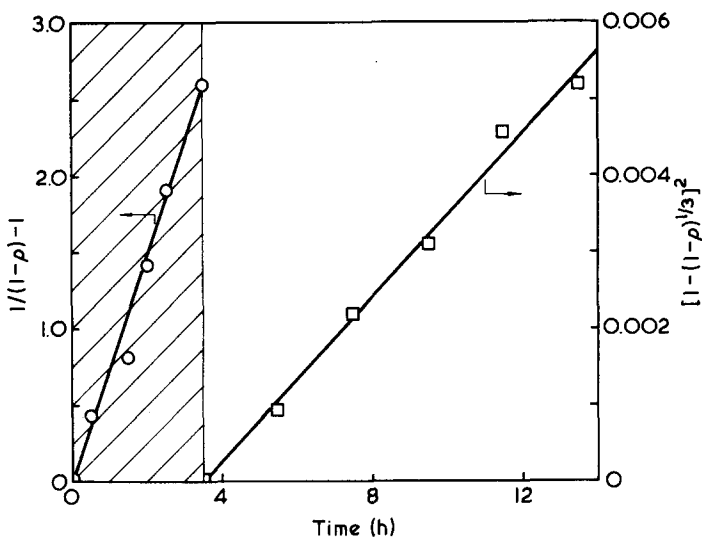**Figure 3** Plots of conversion p ($\bigcirc$) and water-insoluble fraction c_i' ($\square$) vs time at 138°C

Figure 4 Relationships between $1/(1-p)-1$ (second-order kinetics) ($\bigcirc$) and $[1-(1-p)^{1/3}]^2$ (three-dimensional diffusion) ($\square$) vs time at 138°C

The boiling points of n-octane and p-xylene proved to be important limits for the polyamidation reaction studied. Intermediate temperatures were tested by using mixtures of n-octane and p-xylene. In *Figure 5* the progress of the polyamidation reaction at 128°C is shown. Again the existence of an induction period, lasting for about 4h, can be easily noticed. By comparison with *Figure 1*, it is clear that an increase in the reaction temperature by only 2°C results in a considerable increase in polymerization rate. Nevertheless, a transition to the melt state is eventually inevitable and after formation of a

product of higher melting point the reaction medium turns back to the solid state.

By testing the data of the polymerization run at 128°C against the model processes of *Table 1*, the following conclusions were drawn: (a) While the reaction proceeds in the solid state, the model of nucleation and growth ($r^2 = 0.99$), but also the models of Griskey and Lee ($r^2 = 0.99$) and Chen, Griskey and Beyer ($r^2 = 0.99$), fit the experimental data well. Correlation coefficients for the other models are the following: diffusion models, 0.73; phase-boundary-controlled, 0.92; linear kinetics, 0.93; first-order kinetics, 0.92; second-order kinetics, 0.91; and third-order kinetics, 0.90. (b) During the melt stage the reaction proceeds according to second-order kinetics ($r^2 = 0.99$). (c) During the last stage, after solidification, all the diffusion-controlled models fit the corresponding experimental data well ($r^2 = 0.99$), whereas the correlation coefficients for the other models are the following: phase-boundary-controlled models, 0.93; nucleation and growth models, 0.81 and 0.71 ($n = 2$ or 3 respectively); Griskey and Lee model, 0.84; linear kinetics, 0.95; first-order kinetics, 0.95; second-order kinetics, 0.95; and third-order kinetics, 0.95. *Figure 6* shows clearly the good agreement of the data with the nucleation and growth, second-order and diffusion-controlled models during the three stages of the reaction, solid–melt–solid respectively.
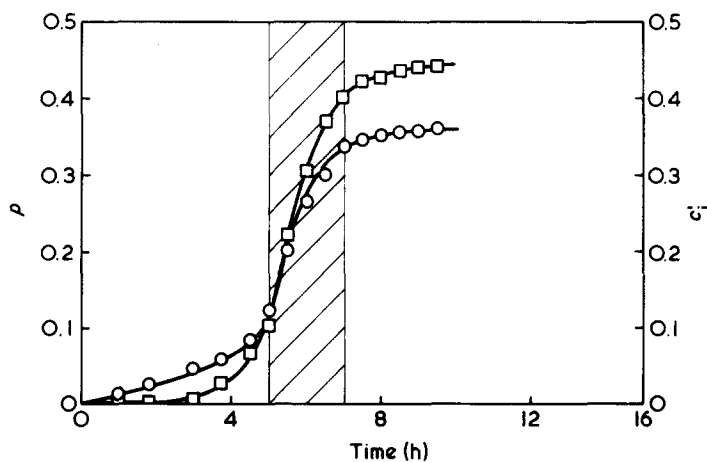

Figure 5 Plots of conversion p ($\bigcirc$) and water-insoluble fraction c_i' ($\square$) vs time at 128°C
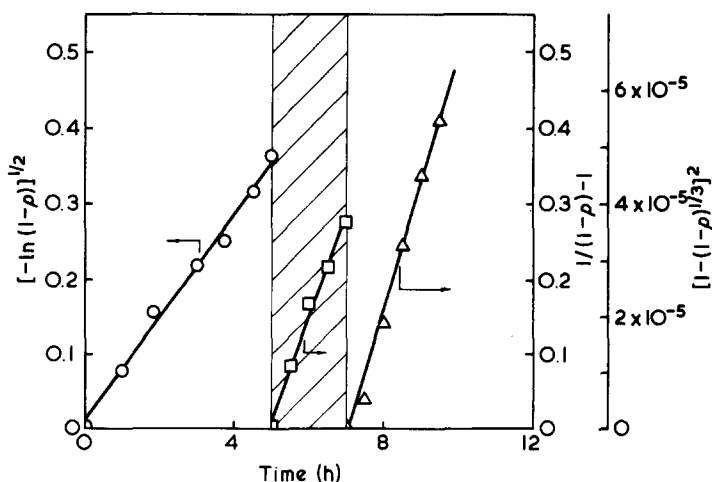

Figure 6 Relationships between $[-\ln(1-p)]^{1/2}$ (nucleation and growth) ($\bigcirc$), $1/(1-p)-1$ (second-order kinetics) ($\square$) and $[1-(1-p)^{1/3}]^2$ (three-dimensional diffusion) ($\triangle$) vs time at 128°C

By increasing the xylene/octane ratio, higher reaction temperatures are effected, but this results in a steep decrease of the time interval before transition to the melt state occurs. Even at 131°C, the process turns to the melt state within less than 30 min. Consequently, the kinetic study of this stage becomes entirely impossible at reaction temperatures higher than 128°–129°C.

Presence of dispersion agents

The solid-state polymerization of dodecamethylene-diammonium adipate is one of the better examples of a process proceeding through lower-melting-point intermediates. Such a case has already been referred to in the literature by Kampouris, who studied the solid-state polymerization of hexamethylenediammonium maleate[20]. The presence of dispersion agents results in a sufficient suspension throughout the course of the reaction, especially when the particles become sticky and tend to agglomerate. Therefore the transitions from the solid to the melt state or even from the melt to the solid state are expected to proceed without agglomeration. The suitability of the following dispersion agents was examined: (a) carnauba wax (crude and decolourized); (b) beeswax; (c) montana wax; (d) dioleamide of diethylene-triamine; and (e) fatty alcohol poly(ethylene glycol) ether.

The efficiency of the dispersion agents was tested at 129°C under the following conditions: (a) reaction time, 4 h; (b) salt to non-solvent ratio, $10 \, g \, l^{-1}$; (c) salt grain size, minus 400 mesh; and (d) amount of dispersion agent, 2% w/v on the inert solvent. The results obtained are given in *Table 2*. As the data indicate, none of the substances tested proved sufficient to prevent agglomeration. They can be distinguished only from the time interval before agglomeration occurs.

Characterization of the polymerization products

The polymerization products were further characterized by viscosity measurements, infra-red spectroscopy and X-ray diffraction.

The polymer products eventually produced according to the routes of *Figures 1, 3* and *5*, after extraction with water, were subjected to viscosity determinations. Intrinsic viscosity values equal to 11.0, 22.0 and 13.0 ml g^{-1} were obtained respectively. As the corresponding reaction time is 24, $13\frac{1}{2}$ and $9\frac{1}{2}$ h, it is clearly concluded that there is also a strong influence of reaction temperature on the molecular size of the resulting polymer. Nevertheless, evaluation of the molecular weight is not feasible due to the absence of any literature information on intrinsic viscosity–molecular weight relationships for nylon-12,6. Subsequently, we attempted to establish such relation-
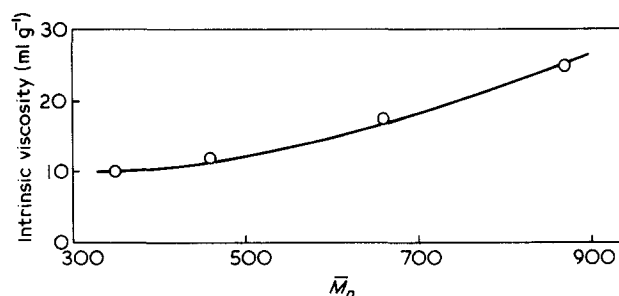

Figure 7 Intrinsic viscosity vs $\bar{M}_n$ curve for nylon-12,6 oligomers

ships within the viscosity range encountered, i.e. up to about $25 \, ml \, g^{-1}$. A number of oligomers were prepared by melt reaction in the presence of varied acid excess. The products of these reactions, after extraction with boiling ethanol (96%) to remove any unreacted species, were subjected to viscosity and cryoscopy determinations. The results obtained are presented in *Figure 7*. Assuming molecular homogeneity, the values K and a of the Mark–Houwink–Sakurada equation were determined as 0.04 and 0.95 respectively (m-cresol, 100°F). Accordingly, after extraction with water, the final products of the solid-state reactions at 126°, 138° and 128°C were calculated to have number-average molecular weights equal to 370, 770 and 440 respectively.

Infra-red spectra of the latter samples showed the characteristic absorptions of polyamides at 3300, 1640 and $1540 \, cm^{-1}$, whereas the absorptions of DMA at 2200, 1660, 1570, 1515, 1410 and $1125 \, cm^{-1}$ were entirely absent. On the other hand, X-ray diffractograms revealed only three strong reflections at 3.7, 4.4 and 19.9 Å. No reflections were noticed at 3.3, 3.9, 4.1, 5.0, 6.8 and 20.1 Å, distances characteristic of dodecamethylenediammonium adipate.

CONCLUSIONS

Solid-state polyamidation of dodecamethylenediammonium adipate is strongly influenced by reaction temperature. The polycondensation proceeds at a marked rate in a temperature range extending up to about 25°C below the melting point of the salt. On the other hand, even at the lower temperatures of this range, the reaction medium turns from the solid to the melt state, resulting in rapid agglomeration of the reacting grains. The agglomeration is not affected by the presence of dispersion agents. Up to the transition point, the existence of an induction period is evident and the experimental data fit the model of nucleation and growth well. During the melt stage, the reaction proceeds according to the second-order kinetics and after solidification, due to the formation of a product of higher molecular weight, the data fit the diffusion-controlled models well, showing a change in reaction mechanism. In addition the differences, in several cases, between equations is less than the experimental error of the data. Consequently, DMA polycondensation, within the overall region of p vs t studied, cannot be described exclusively by any of the models tested. We strongly believe that the true reaction model should be based primarily on the process leading to the transition phenomena observed. The latter may be correlated with the water formed during the reaction and the mechanism of its elimination from the reaction sites.

Table 2 Effectiveness of dispersion agents

Type of dispersing agent	Effectiveness	Time interval before agglomeration (h)
Crude carnauba wax	poor	3½
Decolourized carnauba wax	poor	1
Beeswax	poor	3¾
Crude montana wax	poor	1
Dioleamide of DET	poor	3½
Fatty alcohol poly (ethylene glycol) ether	poor	1⅓

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