

Investigation on solid-state polymerisation reaction mechanism of Nylon-6

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Solid-state polymerisation (SSP) is a convenient method of producing high molecular weight polymers at relatively low temperatures. In this work the SSP of nylon-6 was examined in a fixed-bed reactor. The solid-state polymerisation reaction kinetics of Nylon-6 was investigated in connection with the relative viscosity (RV) of the initial starting materials. The changes in the molecular weight and other properties were monitored as a function of the reaction times at solid-state temperatures of 130–200 °C. Starting materials with higher initial molecular weights exhibited higher rates of SSP than those with lower initial values. Activation energies decreased at temperatures above 170 °C, and this indicated a change in the SSP reaction mechanism. At temperatures of 170–200 °C similar activation energies were required for the polymerisation of all samples.

Keywords: solid-state polymerisation, nylon-6

Polyesters and polyamides (PAs) are important commercial polycondensation polymers, widely used in a variety of applications. In addition to their commanding positions as textile fibres, PAs can be readily processed through extrusion or injection moulding to yield mechanical and electrical parts, while polyesters play an important role in the automotive tyre cord and the bottle market. The conventional solution to melt polymerisation techniques stops at a low or medium molecular weight product, due to problems arising from a severe increase of the melt viscosity and the operating temperatures. Higher molecular weights may be reached by SSP at temperatures between the glass transition temperature and the onset of melting. The synthesis of high quality and high molecular weight polyester and polyamides by SSP is important for tyre cords, packaging materials, technical fibres and engineering plastics.

Polycondensation progresses through chain end reactions in the amorphous phase of the semicrystalline polymer, which in most cases is in the form of flakes or powders; reaction by-products are removed by application of vacuum or by passing an inert gas. The advantages of SSP include low operating temperatures, which restrain side reactions and thermal degradation of the product, while requiring inexpensive equipment, and uncomplicated and environmentally sound procedures. The disadvantages of SSP focus on low reaction rates compared to melt phase polymerisation, and possible solid particle processability problems arising from sintering.¹⁻³

The polycondensation rate depends on both chemical and physical processes. Depending on the process and operating variables, the overall SSP rate is controlled by one or more of the following steps^{1,4,5}:

- (1) Diffusion of the molecular chain end groups in the solid phase
- (2) Reversible chemical reactions between the molecular chain end groups.
- (3) Diffusion of the volatile by-products in the solid polymer.
- (4) Diffusion of the volatile by-products from the polymer surface to the inert gas.

A large number of parameters are reported to affect the SSP overall rate and define the relevant rate-determining step. The main factors include the reaction temperature, initial end group concentration, particle geometry, gas flow rate and crystallinity. The reaction temperature is probably the most important factor in SSP, due to its interaction with almost all other aspects of the process.⁵⁻⁸ The role of the SSP temperature is significant, as it may influence the limiting step of the

process and may cause changes in the controlling mechanism, with a resulting change of the reaction activation energy.⁹

The dependence of the reaction temperature on the intrinsic SSP rate constant is indicated by the values of the SSP activation energy (E_a), reported to be between 10.5 and 81.5 kcal mol⁻¹ in the case of PAs, and 15.0–42.5 kcal mol⁻¹ for polyesters. In general, the reported SSP values are slightly higher than those for melt processes.^{2,10,11} With PET, the polycondensation equilibrium constant (K_{eq}) used in SSP studies is similar to that for the melt process.¹² For polyamides, the K_{eq} is a function of the reaction temperature. More specifically, in the case of SSP to prepare polycapraamide (PA-6),^{13,14} at given water content, the amide equilibrium constant is described by Eqn (1), where the enthalpy of reaction is -7.6 kcal mol⁻¹, revealing an exothermic reaction. Another pertinent equation (Eqn (2)) has been suggested by Gupta and co-workers.^{15,16}

$$\log K_{eq} = \left[\frac{1761.4}{T} - 0.6614 \right] \quad (1)$$

$$K_{eq} = \exp \left[\frac{3.9842 + \frac{2.4877 \times 10^4}{T}}{R} \right] \quad (2)$$

where K_{eq} is the equilibrium constant for polycondensation of PA-6, T is the absolute temperature and R is the universal gas constant.

The polymerisation reaction and diffusion of the reaction by-products usually occur simultaneously. The decoupling of the by-product diffusion from the reactions could, therefore, be an additional factor that complicates analyses of the SSP kinetics. The estimation of diffusivities of by-products is not easily accomplished because several diffusion processes take place simultaneously as reaction occurs, making the determination of the individual rate constants more complicated. Although the kinetic analyses based on each mechanism help to clarify what is happening during the SSP process, they are not always feasible or appropriate, especially when comparative studies of the SSP rates are performed. Rate-determining mechanisms can change according to reaction conditions and are often unknown under a certain set of conditions. For the purpose of a comparative study, it would, therefore, be helpful to obtain apparent rate constants that can be used without assumption concerning the reaction mechanisms, rather than to use the complicated models that have been made based on assumptions about SSP mechanisms. In this manner, relative viscosities (RVs) or molecular weight data have been plotted as function of the square root of SSP time by several researchers.^{6,7,16-20}

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This method of plotting has often been used in kinetic analyses, in which a diffusion step is involved in the process. These plots yield apparent SSP rate constants, regardless of SSP times, which are convenient to compare even though they do not give fundamental information about SSP mechanisms.

Experimental

Bench-scale SSP system

The SSP system was composed of a reactor, preheater, nitrogen cylinder, temperature controller, and gas flowmeter. The solid-state polymerisation was conducted in a stainless steel vessel fixed-bed reactor 3 cm in diameter, 30 cm long, and fitted with a ceramic filter at the bottom. Through this filter, oxygen-free preheated nitrogen gas flowed into the reactor at a rate of 3 l min⁻¹. The flowing gas warmed up the particles evenly and carried away the condensate (water). The sample could be inserted before warming up the reactor. The temperature in the reactor could be controlled to 0.5 °C. After the loaded reactor was placed in the oil oven, a 40 min stabilisation time was required for the material to reach the desired temperature. The reaction time was counted from the time the material temperature was 2 °C lower than the desired temperature. After each reaction was completed, the reactor was removed from the oven while being purged with nitrogen and cooled by an external air fan. Nitrogen purging was continued until the resin had cooled to less than 60 °C. The samples were then removed from the reactor and subjected to further analyses.

Material and analyses

Three commercial Nylon-6 precursors were made and provided by Ninth Chemical Fibre Factory (Shanghai, China). They had different RVs. Sample A had a RV of 2.23, sample B had a RV of 2.46, and sample C had a RV of 2.77. All the precursors had similar pellet sizes. The RV of nylon-6 for the prepolymer chips and the SSP samples was determined from a 1 % solution in 90 % formic acid as a solvent at 25 °C with an Ostwald viscometer. The concentration for the measurement of RV for the SSP of the nylon-6 samples was 0.11 g ml⁻¹. The number average molecular weight was determined using the following equation⁶:

$$\bar{M}_n = 11500 (\eta_r - 1) \quad (3)$$

$$\eta_r = RV$$

Differential scanning calorimetry

The melting points of the samples were determined using DSC data. A TA Instrument DSC-2010 was used and samples of 8-10 mg were used. The samples were heated from 25 to 260 °C at the rate of 10 °C min⁻¹.

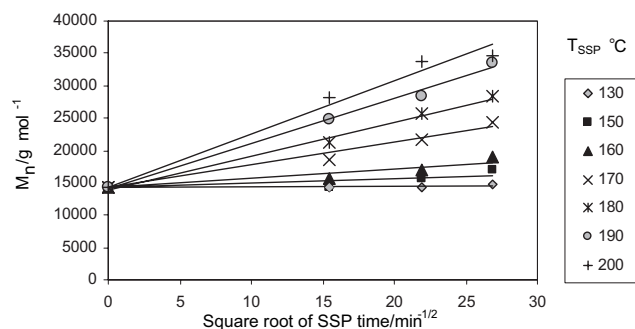


Fig. 1 M_n as function of the square root of the SSP time for precursor A with $RV_0 = 2.23$.

Table 1 Comparison of apparent rate constants

SSP temperature/°C	$k/g \text{ mol}^{-1} \text{ min}^{-1/2}$		
	$RV_0 = 2.23$	$RV_0 = 2.46$	$RV_0 = 2.77$
130	8.14	38.1	44.9
150	69.2	125	137
160	144	224	274
170	349	369	396
180	525	516	542
190	697	666	645
200	825	730	698

Results and discussion

A series of SSP experiments was conducted with three precursors with different RVs (2.23, 2.46 and 2.77) at temperatures ranging from 130 to 200 °C and for reaction times of 4, 8 and 12 h after the material temperatures were 2 °C below the desired temperature. Figure 1 shows the increase in M_n as a function of the square root of the SSP reaction time for precursor A ($RV_0 = 2.23$). Most of the data fit linearly against the square root of time. The other cases of precursors B and C also exhibit similar behaviour.

The slope of each line gives the apparent rate constant ($g \text{ mol}^{-1} \text{ min}^{-1/2}$) at each temperature, as shown in Table 1. It was found that, as the precursor's RV increased, the rate constants (k) also increased. Figure 2 shows the effects of the different RV_0 on the reaction rates for three precursors A, B and C at the temperature of 180 °C.

With a larger RV_0 , the sample may reach a higher molecular weight at the end of the reaction. This fact is based on end group to end group distance distribution. As with higher molecular weight polymers from melt, when taken for SSP they have a homogenous distribution of end group to end group and those with the minimum possible distance between them give rise to faster reactions. This result supports the results obtained by Gaymans *et al.*²¹ and others.^{4,6,8,18-20}

The activation energy (E_a) and frequency factor (A) values, given in Table 2, were determined from the slopes and intercepts of Arrhenius plots (Fig. 3) according to the following equations,¹⁷ in which values for k are the apparent rate constants given in Table 1:

$$k = A \exp\left(-\frac{E_a}{RT}\right) \quad (4)$$

$$\ln k = \ln A - \frac{E_a}{R} \left(\frac{1}{T}\right) \quad (5)$$

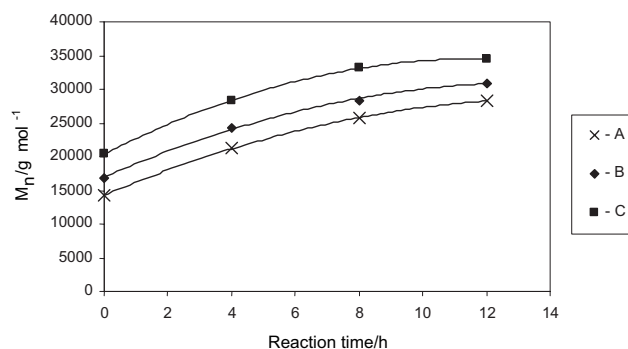


Fig. 2 Effect of starting molecular weight on progress of reaction at 180 °C (A) $M_n = 14000$, (B) $M_n = 16000$, and (C) $M_n = 20000$.

Table 2 Frequency factor (A) and activation energy (E_a).

Precursor	Low temperature (130–170 °C)		High temperature (170–200 °C)	
	A /g mol ⁻¹ min ^{-1/2}	E_a /kcal mol ⁻¹	A /g mol ⁻¹ min ^{-1/2}	E_a /kcal mol ⁻¹
A ($RV_0 = 2.23$)	8.69×10^{18}	33.2	2.96×10^8	12.0
B ($RV_0 = 2.46$)	3.63×10^{12}	20.3	2.22×10^7	9.65
C ($RV_0 = 2.77$)	2.43×10^{12}	19.8	3.04×10^6	7.83

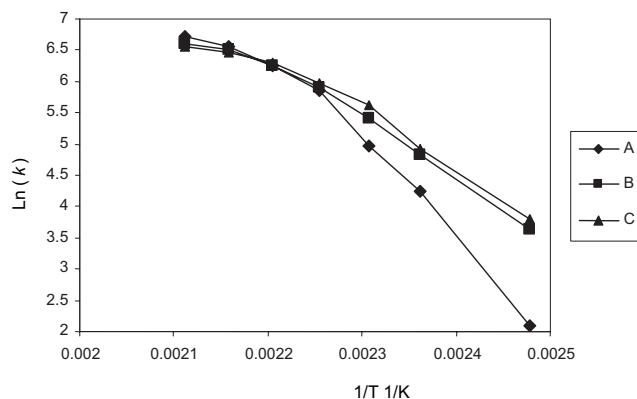


Fig. 3 Arrhenius plot for the SSP of precursors with different RV_0 .

The changes in the slopes, as shown in Fig. 3, were observed according to the temperature region. This slope change is most clear for precursor A ($RV_0 = 2.33$) and indicates that a change in the SSP mechanism occurred as the temperature exceeded 170 °C. When the temperature was higher than 170 °C, activation energies for the three precursors were similar at 7–11 kcal mol⁻¹. When the SSP reaction temperature was lower than 170 °C, activation energies increased to 19–20 kcal mol⁻¹ for precursors B and C. For precursor A, the activation energy significantly increased to 33 kcal mol⁻¹. The frequency factors and activation energies increased as the precursor RV decreased in the low temperature region of 130–170 °C. In the high temperature region of 170–200 °C, however, similar values for the frequency factor and the activation energy were shown for all precursors.

It is clear that the chemical reaction rate, interior diffusion and surface diffusion of by-products have a close relationship with the reaction temperature. Also it is generally found that by-product diffusion is the rate-controlling step as the SSP temperature increases, whereas the chemical reaction is the rate-controlling mechanism when the temperatures are low.^{4,6,7,16} The rate of chemical reaction can be affected by the diffusion rate of chain end groups because of its effect on their mobility. Comparing the values of the activation energy and frequency factor for each precursor in those temperature regions it was inferred that the by-product diffusion step and the diffusion of chain end groups act together as rate-determining mechanisms. The entropy change (ΔS) can be calculated from the following relationship for the reaction kinetics:⁵

$$A = \frac{k_B T}{h} e^{(\Delta S/R)} \quad (6)$$

$$\Delta S = R \ln(Ah / k_B T)$$

Where A is the frequency factor from the Arrhenius equation; h is Planck's constant, which is 6.62×10^{-27} erg; k_B is Boltzmann's constant, which is 1.38×10^{-16} erg; and R is the gas constant, which is 1.987 cal

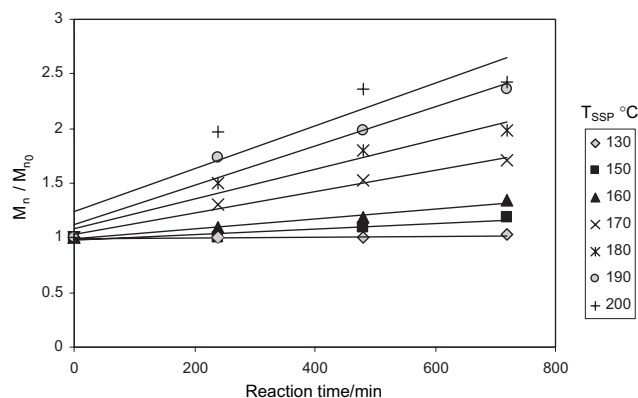


Fig. 4 Plot of M_n/M_{n0} as a function of SSP time for the precursor A.

Table 3 Comparison of rate constants for precursors

SSP temperature/°C	k/h^{-1}		
	$RV_0 = 2.23$	$RV_0 = 2.46$	$RV_0 = 2.77$
130	0.0016	0.006	0.006
150	0.0132	0.0195	0.0181
160	0.0264	0.034	0.0342
170	0.0622	0.0544	0.0485
180	0.0904	0.0767	0.0663
190	0.1212	0.0974	0.0771
200	0.143	0.106	0.0836

mol K⁻¹. The frequency factors in Table 2 cannot directly be used for Eqn (6) because they were obtained by the plotting of molecular weight values against the square root of time and, therefore, have different units. The ratio M_n/M_{n0} can be plotted against the SSP time for precursor A, as shown in Fig. 4.

These data fit well only at low temperature, especially those lower than 170 °C. At higher temperatures, the data do not fit on the straight line, indicating that diffusion processes affect SSP kinetics so that the reaction becomes more reversible. Similar behaviour was observed for precursors B and C.

The slopes of the fitted lines give the apparent rate constants, which are summarised in Table 3. As shown in Fig. 5, an Arrhenius plot can be made from these apparent rate constant values and SSP temperatures.

The activation energies and the frequency factors can be obtained from the slope and the intercept in an Arrhenius plot. Activation energies and entropy changes were calculated for three precursors, as shown in Table 4. Similar but slightly higher activation energies were obtained for each precursor than when the data were plotted against the square root of time. The differences in the activation energy can be related to the fact that kinetic behaviours digress from linearity as the SSP temperature increases. The application of a linear kinetic analysis to data at 170 °C can be one cause for the differences in the activation energies obtained with the two methods.

As the precursor RV increased (2.23, 2.46 and 2.77), the entropy decreased (−7.99, −36.81 and −38.58 cal mol⁻¹ K⁻¹, respectively) at the low temperature region. According to transition state theory, the activation energy indicates the energy barrier between the reactant state and the transition state, and the entropy can be related to the degree of order in the transition state configuration in the reaction

Table 4 Frequency factor (A), activation energy (E_a) and entropy changes (ΔS) for low-temperature data.

Precursor	Low temperature (130–170 °C)		
	A /s ⁻¹	E_a /kcal mol ⁻¹	ΔS /cal mol ⁻¹ K ⁻¹
A ($RV_0 = 2.23$)	1.59×10^{11}	32.4	−7.99
B ($RV_0 = 2.46$)	7.98×10^4	19.7	−36.8
C ($RV_0 = 2.77$)	3.27×10^4	19.0	−38.6

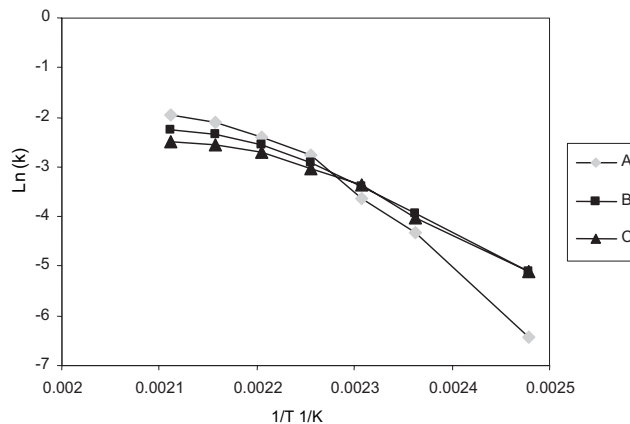
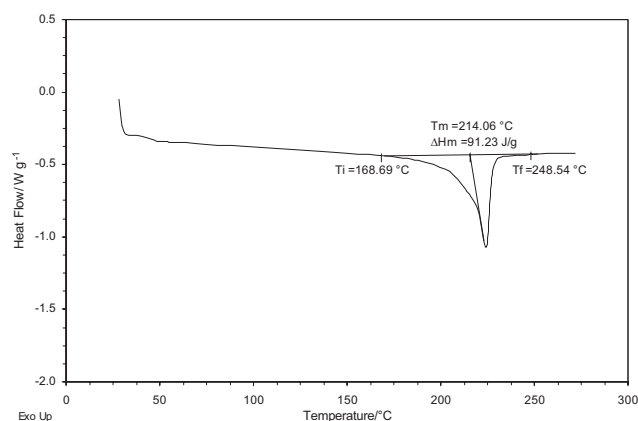


Fig. 5 Arrhenius plot for the SSP of precursors with different RV_0 .

Table 5 The DSC results of precursor A solid-state polymerised at various temperatures

Reaction temperature/°C	T_i /°C	T_m /°C	T_f /°C	ΔH_m Jg ⁻¹
130	177.0	214.1	243.2	129.2
150	177.1	212.4	239.1	128.0
160	180.5	212.4	246.5	126.1
170	186.7	217.7	244.4	113.2
180	186.9	216.8	244.4	111.5
190	186.7	216.7	242.6	102.2
200	187.0	218.6	244.2	91.3

**Fig. 6** DSC thermograms of precursor A before SSP.

path. Considering these results, we can say that, as the precursor RV increased from 2.33 to 2.77, the transition state in the reaction path had lower energy states with more ordered configurations.

DSC studies

The DSC curve of precursor A is shown in Fig. 6 and the results from calorimetric studies of the Nylon-6 chips solid-state polymerised at various temperatures are shown in Table 5.

There is no significant change in the melting temperature with the changes in molecular weight. This is because of the influence of molecular weight on the melting or crystallisation temperatures is significant only for low molecular weight materials.^{4,5} Because the starting material already has a relatively high molecular weight, there is no significant change in the melting point with a further increase in molecular weight.

Conclusion

Nylon-6 precursors of three different RV_0 values were solid state polymerised at temperatures from 130 to 200 °C. The changes in the molecular weights were monitored as functions of the time and temperature of SSP. The kinetics of SSP was dependent on the precursor RV_0 , with faster rates observed for samples with higher RV_0 values.

SSP activation energies were calculated with rate constants obtained as functions of reaction times at polymerisation temperatures of 130–200 °C. These activation energies indicated the temperature dependence of the SSP controlling

mechanisms. Changes in the reaction rates were seen most clearly for precursor A ($RV = 2.33$). As the precursor RV increased from 2.33 to 2.77, change in the activation energies became less obvious. Some phases of the SSP reaction process may include more than one rate-controlling mechanism, and the natures of these mechanisms appear to be influenced by the precursor RV and the reaction temperature.

At SSP reaction temperatures of 170–200 °C, all three precursors displayed similar activation energies. The rate determining mechanisms in this temperature range are thought to include the diffusion of chain end groups, acting together with the more widely acknowledged by-product diffusion mechanism. In the lower temperature range (from 130 to 170 °C), higher activation energies were required for all polymerisations. In this lower temperature range, chemical reactions were the controlling mechanism for SSP of all three precursors. For the material ($RV_0 = 2.33$), end group diffusion appeared to be an additional controlling mechanism.

Received 15 November 2005; accepted 21 November 2005
Paper 05/3620

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