Depolymerization of Nylon 6: Some Kinetic Modeling Aspects

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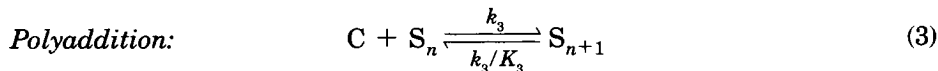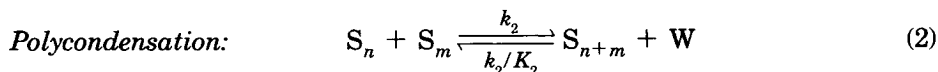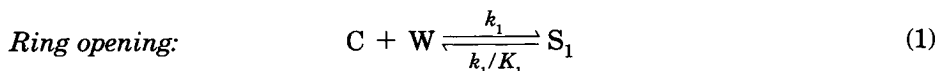
Synopsis

Depolymerization reactions of nylon 6 [poly(ε-caprolactam)] have been modeled based on an existing mechanism for reversible polymerization reactions. The method of moments proposed by Min has been used together with kinetic and equilibrium constants for polymerization reactions to simulate depolymerization reactions. Simulation results thus obtained for batch and semibatch processes compare well with the corresponding experimental results.

INTRODUCTION

In the last few years there has been an increased interest in the area of depolymerization kinetics. Most of this work, however, has been the presentation of experimental results and little effort has gone into analyzing theoretically this process as the exact reverse of the polymerization process. It is therefore proposed in this work to look into the depolymerization reactions, keeping in view the large amount of information available for polymerization reactions. Simulation of depolymerization reactions has been carried out for batch and semibatch reactors, and the results have been compared with experimental results of Smith[1] for batch reactor and those of Takashi et al.[2] for semibatch reactor.

MODELING OF REACTIONS

Simulation of nylon 6 polymerization reactions has been a widely studied subject.[3-9] The hydrolytic polymerization of ε-caprolactam has been modeled in terms of the three main reactions

$$\text{Ring opening:} \qquad C + W \underset{k_1/K_1}{\overset{k_1}{\rightleftharpoons}} S_1 \qquad (1)$$

$$\text{Polycondensation:} \qquad S_n + S_m \underset{k_2/K_2}{\overset{k_2}{\rightleftharpoons}} S_{n+m} + W \qquad (2)$$

$$\text{Polyaddition:} \qquad C + S_n \underset{k_3/K_3}{\overset{k_3}{\rightleftharpoons}} S_{n+1} \qquad (3)$$

where C = ε-caprolactam, W = water, S_n = polymer containing n monomer units, and k_2 = site reactivity.

The only side reaction of importance is the cyclization of linear oligomers. This reaction occurs only to a small extent and hence will not be considered in this treatment.

Polymerization reactions are reversible and consequently reaction model

for depolymerization process too would be represented by eqs. (1)–(3). The reactions would proceed in the reverse direction because of the appropriate concentrations. The rate expressions for various species in a batch reactor can be written as follows[4]:

$$\frac{dC}{dt} = -k_1 CW + \frac{k_1}{K_1} S_1 - k_3 C \sum_{n=1}^{\infty} S_n + \frac{k_3}{K_3} \sum_{n=1}^{\infty} S_{n+1} \tag{4}$$

$$\frac{dW}{dt} = -k_1 CW + \frac{k_1}{K_1} S_1 + k_2 \sum_{n=2}^{\infty} \sum_{m=1}^{n-1} S_{n-m} S_m - \frac{k_2}{K_2} W \sum_{n=2}^{\infty} (n-1) S_n \tag{5}$$

$$\frac{dS_1}{dt} = k_1 CW + \frac{k_1}{K_1} S_1 - 2k_2 S_1 \sum_{n=1}^{\infty} S_n + \frac{2k_2}{K_2} W \sum_{n=2}^{\infty} S_n - k_3 C S_1 + \frac{k_3}{K_3} S_2 \tag{6}$$

$$\frac{dS_n}{dt} = -2k_2 S_n \sum_{m=1}^{\infty} S_m + k_2 \sum_{m=1}^{n-1} S_m S_{n-m} - \frac{k_2}{K_2} W(n-1) S_n$$

$$+ \frac{2k_2}{K_2} W \sum_{m=1}^{\infty} S_{n+m} - k_3 C S_n + k_3 C S_{n-1} - \frac{k_3}{K_3} S_n + \frac{k_3}{K_3} S_{n+1} \tag{7}$$

Initial conditions: Concentrations of all the species C, W, S_n at $t = 0$.

$$q\text{th moment:} \quad M^{(q)} = \sum_{n=1}^{\infty} n^q S_n, \quad q = 0, 1, 2, \cdots \tag{8}$$

$$\frac{dM^{(0)}}{dt} = k_1 CW - \frac{k_1}{K_1} S_1 - k_2 [M^{(0)}]^2 + \frac{k_2}{K_2} W [M^{(1)} - M^{(0)}] \tag{9}$$

$$\frac{dM^{(1)}}{dt} = k_1 CW - \frac{k_1}{K_1} S_1 + k_3 C M^{(0)} - \frac{k_3}{K_3} [M^{(0)} - S_1] \tag{10}$$

$$\frac{dM^{(q)}}{dt} = k_1 CW - \frac{k_1}{K_1} S_1 + k_2 \sum_{r=1}^{q-1} {}^q C_r M^{(r)} M^{(q-r)}$$

$$+ \frac{k_2}{K_2} W \left[\frac{q-1}{q+1} \left(S_1 - M^{(q+1)} \right) + \sum_{r=1}^{q/2,(q-1)/2} (-1)^{r+1} B_r \, {}^q C_{2r-1} \left(M^{(q-2r+1)} - S_1 \right) \right] \tag{11}$$

$$+ k_3 C \sum_{r=1}^{q} {}^q C_r M^{(q-r)} + \frac{k_3}{K_3} \left[\sum_{r=1}^{q} (-1)^r \, {}^q C_r M^{(q-r)} + S_1 \right],$$

$$q = 2, 3, 4, 5$$

Initial conditons: values of moments $M^{(0)} \cdots M^{(5)}$ at $t = 0$.

DEPOLYMERIZATION SIMULATION SCHEME

The rate expressions displayed in eqs (4)–(7) can be integrated over time by finite difference method. Although simple in concept, this method becomes difficult to execute as indicated by the work of Gupta et al.[5] A powerful technique of working with moments of concentrations has been developed by Min,[6] which proves to be very efficient in terms of the com-

putational time. This technique was used by Gupta and Gandhi[4] to simulate polymerization reactions, and their results match within 5% the results of Gupta et al.[5] Min's technique will thus be used in the following simulations.

The method of moments directs attention to integration of various moments rather than individual species concentration. Initial conditions required for the integration are values of the moments which can be generated, with ease, from the initial MWD of the polymer sample. None of the experimental studies, however, report such a complete description of the nylon being used. Usually only number-averaged molecular weights are reported. In order to compensate for the absence of such data, the simulation was conducted as a polymerization process with conditions adjusted to match the reported number averaged molecular weights. The resulting moments of the distribution were then used as the initial values of the moments for the depolymerization simulations. In a typical industrial process the unconverted monomer is removed from the nylon product, and thus the initial concentration of monomer for depolymerization run is set to zero.

Rate constants for nylon 6 reactions are autocatalytic in terms of the acid end-group concentration. The effect of external catalyst, in the case of acid-catalyzed reactions, is thus incorporated by adding its concentration to the polymer acid end-group concentration and using this effective concentration to determine the rate constants. In the semibatch reactor the generated monomer flashes off continuously, and, because of the continuous feed of steam and a constant reactor temperature, the concentration of water is fixed at its solubility in the polymer.

RESULTS AND DISCUSSION

The correctness and effectiveness of the computer simulation can be assessed by a direct comparison with the predictions of Reimschuessel and Nagasubramanian.[7] Figure 1 shows the monomer generation as a function
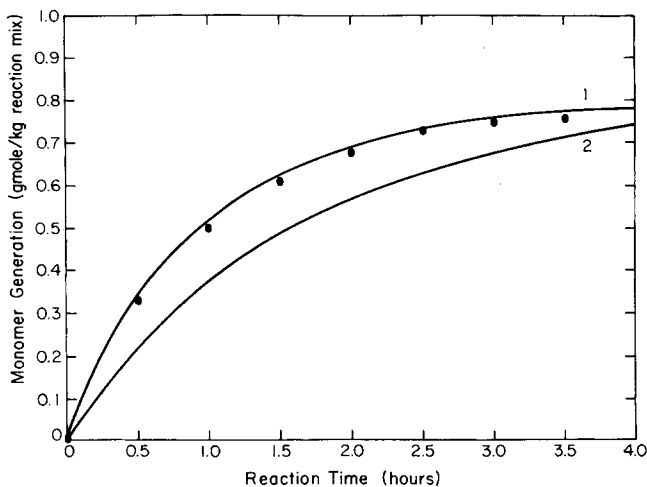

Fig. 1. Hydrolytic depolymerization at 275°C; $P_0 = 140$, $W_0 = 0.111$: (●) predictions of Reimschuessel and Nagasubramanian[7]; (1) simulation results using kinetic constants of Reimschuessel and Nagasubramanian; (2) simulation results using kinetic constants of Tai et al.[9]

of reaction time starting with polymer of number averaged molecular weight of 140 and water concentration of 0.2 wt %. Using the kinetic constants of Reimschuessel and Nagasubramanian, we show that results from this simulation closely match their predictions. However, it has been shown in an independent study by Tai et al.[8,9] that their kinetic constants represent experimental data better than those used by Reimschuessel and Nagasubramanian. Accordingly, the kinetic constants of Tai et al. will be used in this treatment and values obtained by using these constants have also been shown on the same plot.

The early work of Smith[1] on reequilibration of nylon 6 is in effect based on batch hydrolytic depolymerization and has been used for comparison with theoretical studies. Figure 2 shows monomer generation as a function of time at the rection temperature of 250°C. Experimental data are available for two different water concentrations, 0.2% and 1.0%, and the corresponding simulation results have also been plotted. The results show a fair agreement, the simulation results being on a higher side. Theoretical values have been computed for a nylon sample containing equal acid and amine end groups, whereas the nylon samples used by Smith were acid-stabilized. Incorporating this fact in the simulation scheme could lead to better results. The solubility of water in nylon itself is an independent parameter and can be determined from the relationship developed by Fukumoto.[10] Considering the vapor phase to be saturated water vapor, the solubility at the reaction temperature of 250°C is found to be about 0.35 wt %. Thus water above this concentration would exist as a separate phase. In the case of low mass transfer resistance, the concentration of water in the reaction mass will be maintained at the solubility level; the monomer generation for this case has also been shown in Figure 2.

Figure 3 shows monomer generation at the reaction temperatures of 230°C and 270°C. At 230°C water concentration of 0.2% is less than the solubility
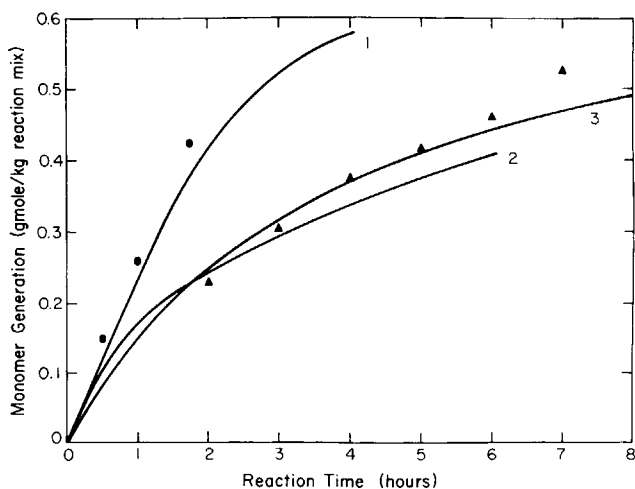

Fig. 2. Hydrolytic depolymerization at 250°C; $P_0 = 126.8$: Experimental data of Smith[1] with water concentrations: (●) 1%; (▲) 0.2%. Solid lines are simulation results with water concentrations: (1) 1%; (2) 0.2%; (3) solubility limited.
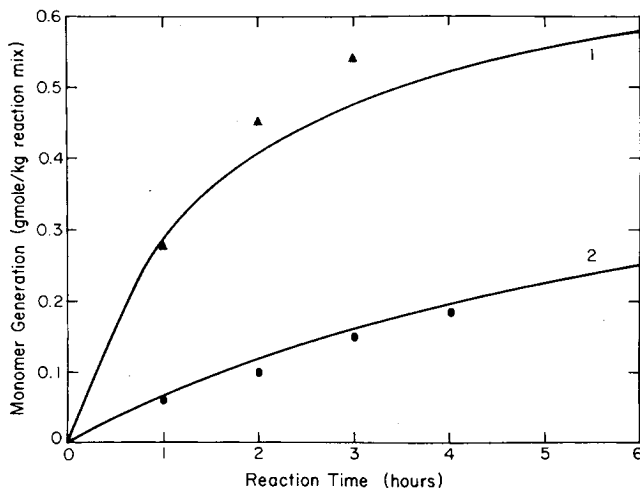
Fig. 3. Hydrolytic depolymerization at 230°C and 270°C; $P_0 = 126.8$. Experimental data of Smith at 0.2% water and temperatures (●) 230°C and (▲) 270°C. Solid lines are simulation results: (1) 270°C and solubility limited water concentration; (2) 230°C and 0.2% water concentration.

value and thus can be used as the actual water concentration. At the higher reaction temperature of 270°C the 0.2% water concentration is more than the solubility of water in nylon. Values have thus been obtained for the solubility limited water concentration and show good agreement with experimental results.

The effect of mass transfer resistance can be minimized in a reactor with good internal mixing, as in the case of the semibatch reactor used by Takashi et al.[2] Figure 4 shows the monomer yield at the reaction temperature of 311°C and catalyst (H_3PO_4) concentrations of 0.56 and 1.05 wt %, and the
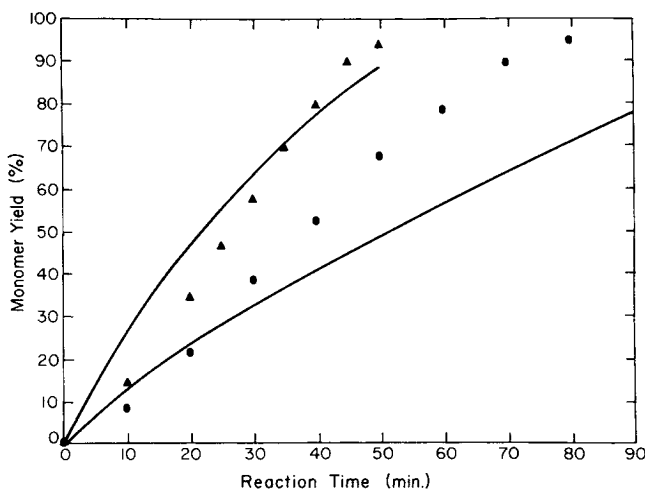

Fig. 4. Acid-catalyzed depolymerization at 311°C. Experimental data of Takashi et al.[2] with catalyst concentration (wt %): (●) 0.56; (▲) 1.05. Solid lines are simulation results with solubility limited water concentration.

agreement with the experimental results is good in the case of 1.05% cat-
alyst.

The gradually increasing slope of the experimental curve could be ex-
plained by the buildup of some equilibrium concentration of monomer in
the reaction mass, which has been neglected in the simulation scheme.
Another reason could be the reaction of acid catalyst with the amine end
groups to form inert caps in the initial stages and ultimate breakdown to
increase the rates towards the end of the reaction period. Thus toward the
completion of reaction there is a good agreement between the simulation
and the experimental results.

At the reaction temperature of 280°C (Fig. 5) there is a significant de-
viation of the simulation results from the experimental values. At this stage
the possibility of thermal degradation complicating the hydrolytic reaction
scheme was looked into. From their experimental studies Luederwald and
Aguilera[11] have found that nylon 6 without catalyst starts to decompose
only above 350°C; this rules out the possibility of thermal mechanisms
dominating at the 280°C temperature conditions. They have also found that
in presence of a catalyst the degradation starts at 280°C and have proposed
a model for the reactions. However, they had considered only basic catalysts
(NaOH etc.) and the model is valid for base-catalyzed degradation (depoly-
merization). Various studies on cationic polymerization have been re-
viewed by Reimschuessel.[12] The studies have shown that both initiation and
propagation of cationic polymerization entail caprolactam cations generated
in an anhydrous medium and the proposed mechanisms cannot be applied
to the present case where reactions are being studied under hydrolytic
conditions.

It should be noted that the water solubility data of Fukumoto has been
reported for nylon 6 containing less than 0.01% external acid as a stabilizer.
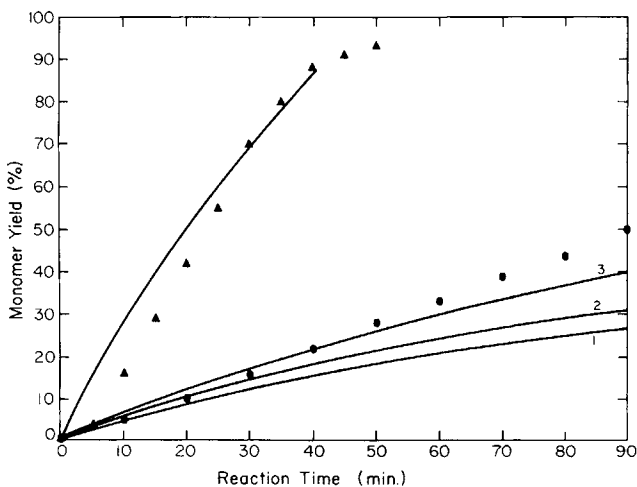Whereas the reactions being considered presently all deal with catalyst

Fig. 5.   Acid-catalyzed depolymerization with H_3PO_4 catalyst concentration of 0.56%. Ex-
perimental data of Takashi et al.[2]: (●) 280°C; (▲) 345°C. Solid lines are simulation results with
water concentrations: (1) solubility limited; (2) 0.2%; (3) 0.5%.

concentration above 0.56%. Water solubility as a function of acid concentration is not available but it might be expected to increase at higher acid concentration. Thus in Figure 5 is also shown monomer generation at higher water concentrations of 0.2% and 0.5% and the simulation results get closer to the experimental ones. This shows the significant effect which water has on the results and places confidence in use of mechanisms for hydrolytic equilibrium reactions.

It has been shown by Rothe et al.[13] that the cationic polymerization rate decreases rapidly above reaction temperatures of 200°C and even below 200°C favorable conditions exist only in the initial phase of the polymerization process. Figure 5 also shows the monomer generation at reaction temperature of 345°C, and in this case agreement between simulation and experimental results is remarkable. Thus it can be asserted that the role of thermal degradation mechanisms in the present situation of hydrolytic depolymerization is minimal.

The above comparisons show the applicability of the model [eqs. (1)–(3)] as well as a method for actual reactor design. The validity of previously mentioned mechanism for acid-catalyzed depolymerization is supported by the general agreement of simulation results with the experimental results, although some specific conditions of the experiments need to be considered in details, in future work. Here it should be noted that in all the experimental studies the polymer samples have been characterized only in terms of the number averaged molecular weight. Although for polycondensation reactions the polydispersity index (PDI) value is expected to be near 2, complete description of the experimental conditions does require the value of PDI, if not the complete MWD.

Modeling of alkali-catalyzed depolymerization has not been treated here, largely due to paucity of experimental data and the inconsistencies existing in the data. Experimental studies of Mukherjee and Goel[14] show that at alkali catalyst (NaOH) concentration of 1.0 wt % the monomer recovery shows a maxima, whereas the experimental results of Takashi et al.[15] show that for any reaction time the recovery is minimum at the alkali (NaOH) concentration of 1.5%. On the other hand, experimental results of Luederwald and Aguilera[11] show that the yield increases initially with increasing catalyst (sodium octanoate, etc.) concentration and then levels off at higher catalyst concentrations. The differences in the above experimental conditions were different molecular weights of the polymer samples and different reaction temperatures. How these differences lead to different roles of the catalyst is not understood.

CONCLUSIONS

Hydrolytic and acid-catalyzed depolymerization reactions of nylon 6 have been modeled based on the hydrolytic equilibrating polymerization reactions and the simulation results show a good overall agreement with the existing experimental values. This shows the validity of the use of polymerization reaction model and kinetic parameters for the case of depolymerization reactions. Better characterization of polymer samples and better specification of experimental conditions would be required for closer agree-

ment of simulation and experimental results. Alkali-catalyzed depolymerization needs to be examined further to provide a better insight into the field of depolymerization as a whole.

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