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A Comprehensive Model for Nylon Melt Equilibria and Kinetics

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ABSTRACT: A model for handling the effect of water on nylon equilibria and kinetics has been developed and tested. Observed variations in the equilibria and kinetics are attributed to microscopic phenomena, not an empirical expression. The equilibrium variation is modeled based on two states of water in the nylon melt, and the kinetic variation is modeled as due to a changing dielectric constant. All reactions are assumed to be acid catalyzed. Results are good at water to polymer ratios ranging from 0.01 to 30 and from temperatures from 200 to 280°C. The model framework also allowed the calculation of interchange rates and ring oligomer concentrations. The model is compared with published data and other proposed models. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 69: 1213–1231, 1998

Key words: nylon kinetics; nylon equilibria; ring oligomers

INTRODUCTION

Because of the importance of nylon 6 and 66 as thermoplastics, a great effort has been made to understand the reaction behavior. In addition to the special features of solid-state polymerization, even ordinary nylon melt polymerizations are complex. For example, with nylon 6 there are two more reactions than just polycondensation: ring opening and addition. These additional reactions even allow the end group concentration to overshoot the final equilibrium value.

Because the polycondensation reaction can be written as reaction 2 of Figure 1, the equilibrium expression for this reaction is

$$K_{eq} = \frac{[\text{water}][\text{amide linkage}]}{[\text{carboxyl end}][\text{amine end}]} \quad (1)$$

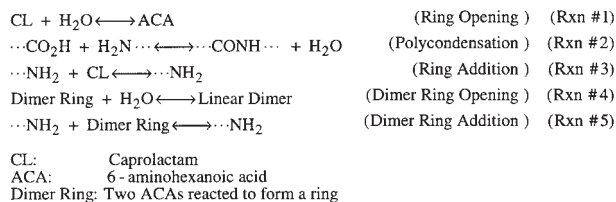Wiloth[1] has shown that measured values of K_{eq} change from about 250 at high water contents to 900 at low water contents. Such variation must be captured by any general model. A similar result was obtained by Ogata for nylon 66.[2] Giori and Hayes[3] explicitly determined the activity of water in a nylon solution; however, even after this correction the equilibrium constant for polycondensation varied significantly with water content.

The kinetic parameters for polycondensation also unexpectedly vary with reaction conditions. For example, in a classic article, Flory[4] showed that polyesterification kinetic behavior varies significantly with conversion. The deviations from expected kinetics were attributed to changes in the mixture dielectric constant.

Lack of a fundamental model for these equilibria and kinetic variations has meant that empiricisms have been developed to describe the observed behavior. Particularly, Ogata[2] and Steppan et al.[5] have developed complex empirical expressions to handle the effects of water content. In some cases, the models seem implausible, as conditions are varied. For example, Ogata's expression predicts that the kinetic rate is infinite when the water concentration is zero. Steppan et al. fit an equilibrium constant expression to data that vary as those of Giori and Hayes[6] do, i.e., with an equilibrium constant that peaks at in-

CL + H$_2$O $\longleftrightarrow$ ACA   (Ring Opening)   (Rxn #1)

$\cdots$CO$_2$H + H$_2$N $\cdots \longleftrightarrow \cdots$CONH$\cdots$ + H$_2$O   (Polycondensation)   (Rxn #2)

$\cdots$NH$_2$ + CL $\longleftrightarrow \cdots$NH$_2$ (Ring Addition)   (Rxn #3)

Dimer Ring + H$_2$O $\longleftrightarrow$ Linear Dimer   (Dimer Ring Opening)   (Rxn #4)

$\cdots$NH$_2$ + Dimer Ring $\longleftrightarrow \cdots$NH$_2$ (Dimer Ring Addition)   (Rxn #5)

CL: Caprolactam
ACA: 6 - aminohexanoic acid
Dimer Ring: Two ACAs reacted to form a ring

Figure 1 Reaction scheme for nylon 6.

termediate water contents. However, Wiloth[7] showed that these data at low water content were incorrect because the authors had not waited long enough for equilibrium. Indeed, better data show that the equilibrium constant at low water content is almost constant and rather insensitive to water.[7] Fitting literature data to empirical expressions also suffers from insufficient precision of data. Tai et al.[8] and Giori and Hayes[6] did almost exactly the same experiment (water = 0.82 mol/kg and 240°C), and found results that differed by more than 10%. Forcing empirical data fits in these situations means that the model will not extrapolate or predict with confidence. In fact, neither Ogata nor Steppan et al. compared their models against data that were not used to fit the model.

The first aspect that all equilibrium models should contain is thermodynamic consistency. For nylon 6, the first three reactions in Figure 1 overspecify the system: reaction 1 followed by reaction 2 is equivalent to reaction 3. This then requires that $\Delta H_1 + \Delta H_2 = \Delta H_3$ (with a similar expression for entropy). In a similar vein, reaction 4 followed by reaction 2 is equivalent to reaction 5. Two authors have fit kinetic and equilibrium expressions for nylon 6 at low water contents.[9,10] The constants of Tai et al.[9] are currently the standard for modeling nylon 6 melt reactions (Table I).

These published constants can be checked to get an idea of the quality of the data fit. Any significant deviation would indicate that a calculated "equilibrium" does not have all forward and re-

verse reactions in balance, as thermodynamics and the principle of microscopic reversibility would require. For the constants of Tai et al.,[9] the enthalpy balance (#1 + #2 = #3) closes to within 16 cal/mol and the entropy balance to within 0.005 cal/mol/°C. The constants of Reimschuessel et al.[10] also balance closely. However, the situation is much worse for the dimer ring opening (#4) and dimer polyaddition (#5) reactions of Tai et al. Calculation of this checksum ($\Delta H_4 + \Delta H_2 = \Delta H_5$) shows the dimer reaction enthalpy balance to deviate by more than 100% (4.5 kcal/mol). In other words, the equilibrium parameters for the reactions of dimer are meaningless. Thus, nylon equilibrium parameters must be constrained to ensure thermodynamic consistency.

The concentration of ring oligomers is also of interest industrially because these materials can degrade the overall polymer properties. Reaction models have been generally in the form of eqs. (4) and (5) in Figure 1. In other words, authors have just extended the standard polyamidation ideas to cyclic oligomer formation. Models based on modern quantitative experimental techniques have come primarily from two groups.[11–13] There does not seem to be a consensus yet regarding the correct way to model these concentrations.

In this article, a new fundamental model is presented that will handle wide ranges in water concentration and temperature variations as well as interchange reactions and ring oligomer formation.

SIMULATION AND PARAMETER ESTIMATION METHODS

All dynamic and equilibrium simulations shown in this report were carried out by using the modeling equations developed in Jacobsen and Ray[14] and implemented in POLYRED, a polymer reaction simulation package. These equations are

Table I   Nylon 6 Constants of Tai et al.[9]

| Reaction (See Fig. 1)	Uncat. Preexp Factor (kg/mol/h)	Uncat. Activation Energy (cal/mol)	Cat. Preexp Factor (kg^2/mol^2/h)	Cat. Activation Energy (cal/mol)	Enthalpy of Reaction (cal/mol)	Entropy of Reaction (cal/mol/°C)
1	5.98×10^5	19880	4.31×10^7	18806	1918.0	−7.885
2	1.89×10^{10}	23271	1.21×10^{10}	20670	−5945.8	0.944
3	2.86×10^9	22845	1.64×10^{10}	20107	−4043.8	−6.946
4	8.58×10^{11}	42000	2.33×10^{12}	37400	−9600.0	−14.52
5	2.57×10^8	21300	3.01×10^9	20400	−3169.1	0.5827
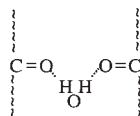
Figure 2 Water bridge between carbonyl linkages in nylon polymer.

quite extensive and will not be repeated here. The new fundamental equilibria and kinetic expressions developed here were incorporated directly into these modeling equations. Parameter estimation was performed using associated estimation software, GREG, developed in the research group of Prof. W. E. Stewart.

DEVELOPMENT OF MODEL—EQUILIBRIUM

There are then several features that a new model must contain. It must be easy to calculate. Large numbers of new reactions will make the model confusing to the user and are difficult to implement. The new model should account for variations in the equilibrium constant due to changing water concentrations. Additionally, the model should be comprehensive with a minimum of constants. This enhances the precision of any constant and gives more confidence when the model is being extrapolated.

Two approaches to the variation of the equilibrium constant have been reported in the literature: activity coefficients and empirical fits. In this work, a third, more fundamental approach, is used. Water in the nylon melt is considered to exist in one of two states: bound (Fig. 2) and free. Bound water is hydrogen bonded to the carbonyl group in nylon polymer as shown in Figure 2. "Free" water is simply unbound water.
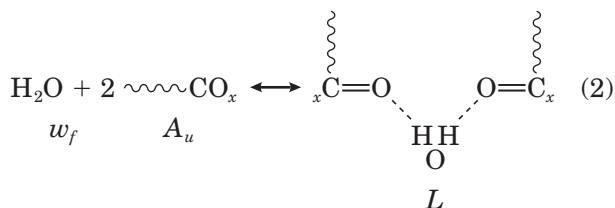
The idea of a water bridge stems from the room temperature water sorption work of Puffr and Sebenda,[15] who studied a series of nylons (2–11) and found for the higher nylons (nylon 8+) the molecular structure would absorb about 0.5 molecules of water per amide group in the amorphous region. Because water is known to hydrogen bond strongly to carbonyl groups, Puffr and Sebenda hypothesized the water to exist in the bridge form shown in Figure 2. The same research found the lower nylons to have a higher saturation level, between 1.0 and 1.5 water molecules per accessible amide group. This additional water will not be considered in the proposed model because only the most stable water will continue to be sorbed
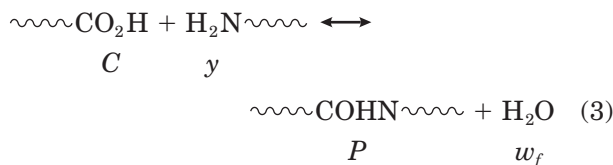
at reaction temperatures of $\sim 230°C$ compared to Puffr and Sebenda's experiments, which were at 20°C. Puffr and Sebenda further cite the work of Kawasaki and Sekita,[16] who found a marked change in the mobility of water in nylon 6 as measured by NMR when the water concentration moved through the 0.5 mol/mol of accessible amide group range. This qualitative difference implies a structural change as the water concentration exceeds that which water bridges could consume.

Independently, Goldbach[17] hypothesized a similar idea based on the dynamical-mechanical response of nylon 6. An additional relaxation appears when water is added to the sample. This is interpreted by first noting that the water also changes the IR signal of the nylon carbonyl group, implying some hydrogen bonding. Next, if the relaxation spectrum is changed when water is added, then there must be changes in the interactions between chains. So, Goldbach supposed that these data were consistent with water bridge formation.

The data discussed above relates to water at room temperature, far removed from the reaction conditions. Fukumoto[18] examined the solubility of water in nylon 6 melts ($\sim 240°C$). Here, the enthalpy of sorption was observed to be -18.3 kcal/mol. *Ab initio* investigation of the interaction energy between N-methyl acetamide and water allowed the interaction enthalpy for one hydrogen bond to be estimated at approximately -9.4 kcal/mol (using Gaussian 92; for more details see Mallon[19]). Because merely doubling this number would mean that some interactions are counted twice, the enthalpy of formation of two hydrogen bonds, a water bridge, is approximately -17 kcal/mol. The agreement between the *ab initio* calculations and Fukumoto's enthalpy of sorption is reasonable and further motivates the idea of a water bridge.

Because this model contains two states for water, a single equilibrium expression [eq. (1)] is no longer sufficient. Instead, the following two reactions are assumed to occur, and the equilibrium is calculated based on these (because enthalpy and entropy are state functions, the kinetic path does not matter).

$$\sim\!\!\sim\!\!\sim CO_2H + H_2N\!\sim\!\!\sim\!\!\sim \longleftrightarrow$$
$$\quad C \qquad y$$

$$\sim\!\!\sim\!\!\sim COHN\!\sim\!\!\sim\!\!\sim + H_2O \quad (3)$$
$$\quad P \qquad\qquad w_f$$

The first reaction forms a water bridge complex (L in Fig. 2) from free water (w_f) and two dry carbonyls (A_u) (either polymer or carboxyl). Because the water bridge can form with either a carbonyl linkage or a carboxyl end, the x in eq. (2) represents either continued polymer chain ($HN\!\sim\!\!\sim\!\!\sim$) or the carboxyl end (OH). Equation (2) can also be understood as the sum of two elementary steps, where L^* represents the formation of one hydrogen bond between water and a carbonyl. L^* then reacts with another carbonyl to form the bridged complex.

$$w_f + A_u \leftrightarrow L^*$$
$$L^* + A_u \leftrightarrow L$$
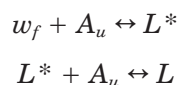
Although each step leads to the formation of one hydrogen bond (meaning that the enthalpies should be similar), the entropy of reaction for each step should differ greatly. In the first step, the water losses its translational freedom (a large negative change in the entropy). By contrast, the second step would just involve the formation of the second hydrogen bond with only a small loss of entropy. Approximate equilibrium constants for the two steps can be generated by using the fitted value for the overall equilibrium constant for eq. (2) (Table II) and by assuming that the equilibrium constant for the second step is just exp $(-\Delta H/RT)$ where ΔH is the enthalpy of forming one hydrogen bond (about 9.4 kcal/mol). This process determines equilibrium constants on the order of 10^{-6} and 10^{4} for the first step and second step, respectively. In other words, L^* is more like a transition state than a stable intermediate. In addition, the representation of eq. (2) requires two fewer estimated constants. For these reasons, eq. (2) will be used to find the relative populations of bound and free water.

Equation (3) represents the standard polyamidation reaction between an acid group (C) and an amide group (y) to form polymer (P) and free water (w_f). From eqs. (2) and (3), two equilibrium expressions can be formed as

$$K' = \frac{L}{A_u^2 w_f} \quad \text{and} \quad K'' = \frac{P w_f}{y C} \quad (4)$$

Two other variables used in this derivation are w_{tot}, the total water concentration in the melt, and A_{tot}, the total concentration of carbonyl groups in the melt. A simple water balance gives

$$L = w_{\text{tot}} - w_f \quad (5)$$

Implicit in eq. (4) is the idea that the probability of a type of carbonyl (carboxyl or polymer linkage) participating in a water bridge is based on its relative concentration. This assumption means that the ratio of saturated polymer linkages (P_s) to unsaturated ones (P_u) is the same as the ratio of total saturated carbonyls (A_s) to unsaturated ones (A_u). This leads to the following useful relations and definitions:

$$\frac{P_s}{P_u} = \frac{A_s}{A_u}$$
$$A_{\text{tot}} = A_u + A_s$$
$$A_s = 2L \quad (6)$$

By substituting eqs. (5) and (6) into the expression for K', an expression for the free water concentration can be developed

$$K' = \frac{(w_{\text{tot}} - w_f)}{(A_{\text{tot}} - 2w_{\text{tot}} + 2w_f)^2 w_f} \quad (7)$$

This is a cubic equation in free water concentration and can be solved by standard methods. Where multiple roots exist, only one makes physical sense.

A method of solution of nylon equilibria is almost complete. To handle nylon 6, however, ring addition (reaction 3 of Fig. 1) must also be considered. The ring addition reaction is not affected by water because water is not involved in the reaction and so the concentration of free water does not matter. Because of the overspecification of the nylon 6 system with three reactions (see the discussion associated with Table I), the ring (caprolactam) concentration is specified by eq. (8); the equilibrium expression for the ring addition reaction (the ring opening reaction is not necessary).

$$K_{\text{add}} = \frac{[\text{Amine}^{2+}]}{[\text{Amine}][\text{Caprolactam}]} \quad (8)$$

Here, the "2+" means that only amines that are connected to polymer chains of a degree of polymerization of two or more should be included.

Table II   Results of Nylon Batch Polymerization Parameter Estimation

Fitted Equilibrium Parameters

Enthalpy of polycondensation reaction (without any hydration occurring)	404.13 cal/mol
Entropy of polycondensation reaction (without any hydration occurring)	12.503 cal/mol/°C
Water sorption preexponential factor	1.78×10^{-10} L^2/mol^2

Assumed Equilibrium Parameters

Enthalpy of water sorption	18,300 cal/mol
Enthaly of polyaddition	−4043.8 cal/mol
Entropy of polyaddition	−6.9457 cal/mol/°C

Fitted Kinetic Parameters

Rate of polycondensation at 230°C (before accounting for dielectric effect)	0.007065 L^2/mol^2/h
Activation energy for polycondensation	8578 cal/mol
Rate of polyaddition at 230°C	0.01108 L^2/mol^2/h
Activation energy for polyaddition	1754 cal/mol
Rate of ring closing at 230°C	0.03514 L/mol/hr
Activation energy for ring closing	3411 cal/mol
Dielectric kinetic parameter	40,716 cal/mol
Preexponential factor for polymer dielectric constant	.06681
Initial monomer conc. for	
Giori and Hayes data set[6]	0.00195 mol/kg
Wiloth's data set[22]	0.00480 mol/kg
Data set of Tai et al.[8]	0.00284 mol/kg

Assumed Kinetic Parameter

Exponential term for dielectric constant	4041 cal/mol

Equation (9) calculates this concentration with a knowledge of the monomer concentration (P_1).

$$[\text{Amine}^{2+}] = [\text{Amine}] - [P_1] \qquad (9)$$

If K' and K'' are both assumed to have an enthalpy and entropy of reaction, then four parameters are needed to specify the system.

RESULTS OF MODEL—EQUILIBRIUM

The parameter K' represents the formation of a water bridge in nylon. If the sorption from the gas phase at low partial pressures involves quantitative formation of water bridges, then the enthalpy of sorption should be the same as the enthalpy of the water bridge formation. The experimental value of enthalpy for water sorption (−18.3 kcal/mol)[18] was used to reduce the number of fitted parameters. This left three parameters for nylon 66: the preexponential factor for water sorption

(another way of specifying the K' reaction entropy) and two parameters for K'' [eq. (10)]. Finally, for nylon 6 reactions, K_{add} is also defined with an enthalpy and entropy of reaction [eq. (10)] (a total of five parameters).

$$K' = A \exp\left(\frac{18,300}{RT}\right),$$

$$K'' = \exp\left(\frac{-\Delta H'' + T\Delta S''}{RT}\right),$$

$$\text{and } K_{add} = \exp\left(\frac{-\Delta H_{add} + T\Delta S_{add}}{RT}\right) \quad (10)$$

To compare the model described above to experimental data, the experimental results of Ogata,[2,20] Wiloth,[1,21,22] Giori and Hayes,[6] and Tai et al.[9] were collected. These data sets represent the polymerization of nylon 6, 66, and 7 at temper-
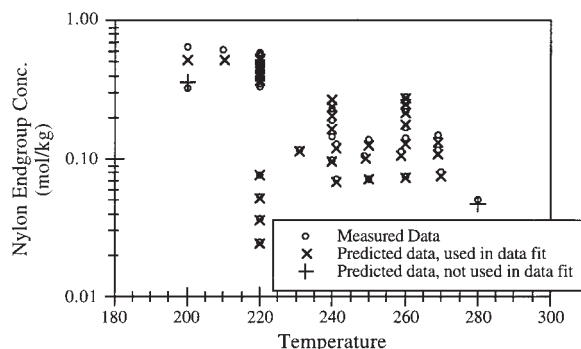
Figure 3 Comparison of model to experiment for nylon equilibrium, data of Ogata,[2,20] Wiloth,[1,21,22] Giori and Hayes,[6] and Tai et al.[9] (End groups are of a single type.)

atures from 200–280°C. Modeling of nylon 6 required two more constants (for K_{add}). Because water is neither a reactant nor a product in the polyaddition reaction, as long as the caprolactam activity coefficient is relatively constant, equilibrium parameters for this reaction should be invariant with water concentration. Furthermore, because the parameters estimated by Tai et al. appear to be reasonable for caprolactam conversion at equilibrium, these constants[9] for the enthalpy and entropy of polyaddition (Table I) were used to calculate K_{add} in eq. (10). Values for the equilibrium model parameters are summarized in Table II.

Figure 3 compares model predictions with experimental data points. Each circle is an experimental point of one of the researchers mentioned above. For each experiment, there are two independent variables (temperature and water content) and one dependent variable (end group concentration). The water content for each of the batch polymerizations is on an orthogonal axis (not shown). The experimental data (shown by $\bigcirc$s) were used to estimate the parameters for the model, and those parameters along with the appropriate temperature and water content were used to predict the end group concentration. For an exact model, the predicted end group concentration (shown by the $\times$s and +s) would exactly overlay each circle. As can be seen, the model is reasonable over 1.5 orders of magnitude in end group concentration and over the entire temperature range. Additionally, the model was tested with some data that were not used in the parameter estimation step; the large plus signs denote the model predictions here. These predictions agree well with the data, and the entire range of

nylon equilibrium data is then consistent with the model.

One of the major goals of the proposed model is to handle the effect of water concentration on the apparent equilibrium constant for nylon. Figure 4, data of Wiloth, shows how the experimental and the predicted "apparent" equilibrium constants vary with water content. The predicted "apparent" equilibrium constants shown in Figure 4 were calculated by determining the equilibrium end group concentrations predicted by the model at a variety of water concentrations. By substituting these into eq. (1), the "apparent" constant was generated. The same procedure was followed with the experimental points; the experimental equilibrium values were substituted in eq. (1). In Figure 4, the model and the data compare well. The deviation at higher water contents can be attributed to not accounting for ring oligomers (treating them as polymer) and to nonequilibrium conditions at the time the "equilibrium" point was taken. The kinetic model, discussed in the next section, predicts longer times to equilibrium than Wiloth waited.

The deviation at intermediate water contents is attributed to a simplification in the two state model. Kurosaki[23] found that water sorbed into silica gels exists in three (not two) states (Fig. 5). One is very tightly bound with a dielectric constant like that of ice; this state is similar to that discussed earlier for nylon (Fig. 2). The second has a dielectric constant about half of that of free water. This is consistent with the water being absorbed on a polymer segment in a random direction. The last is free water with a dielectric constant identical to free water. Presumably, the analysis presented here has oversimplified the problem by just having two states. However, two more parameters for an enhanced model with three states would be needed. We choose to model
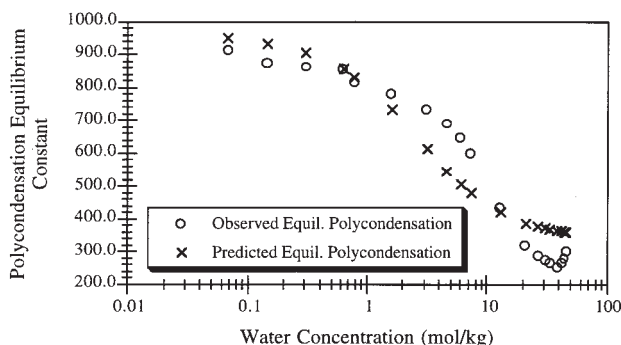

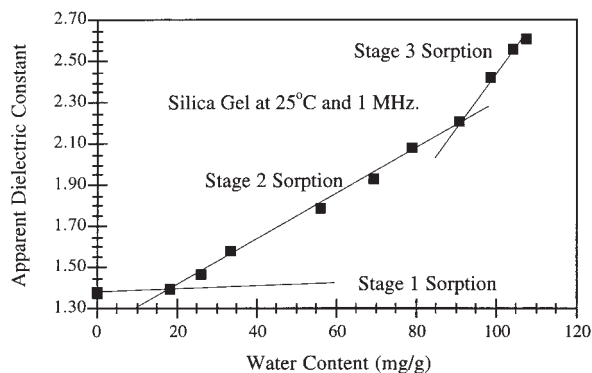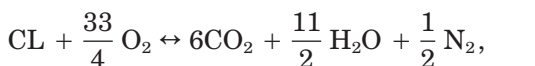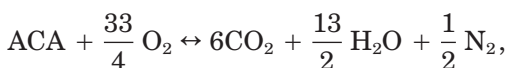**Figure 4** Effect of water on equilibrium constant: model and data of Wiloth.[1]

Figure 5 Effect of the dielectric constant due to water sorption in silica (Kurosaki[23]).

two states while still retaining reasonable model fidelity.

A further way to examine the estimated constants is to look at data not directly related to polymerizations. Strepikheev et al.[24,25] did combustion experiments to determine the heat of combustion of caprolactam (CL) and 6-aminocaproic acid (ACA) at 20°C. By combining these expressions, the enthalpy of ring opening can be calculated.

$$CL + \frac{33}{4} O_2 \leftrightarrow 6CO_2 + \frac{11}{2} H_2O + \frac{1}{2} N_2,$$

$$\Delta H = -861.6 \text{ kcal/mol}$$

$$ACA + \frac{33}{4} O_2 \leftrightarrow 6CO_2 + \frac{13}{2} H_2O + \frac{1}{2} N_2,$$

$$\Delta H = -855.9 \text{ kcal/mol}$$

$$\therefore CL + H_2O \leftrightarrow ACA,$$

$$\Delta H = -5.7 \text{ kcal/mol (Ring opening)} \quad (11)$$

Furthermore, as mentioned above, by knowing $\Delta H_1 + \Delta H_2 = \Delta H_3$ with reaction numbers defined in Figure 1, the model, with coefficients from Table II, predicts an enthalpy of ring opening of -4.4 kcal/mol. By contrast, Tai et al.[9] and Reimschuessel et al.[10] found enthalpies of ring opening of 1.9 and 2.1 kcal/mol, respectively. The ring opening enthalpy of this work (-4.4 kcal/mol) compares reasonably well with the experimental value of -5.7 kcal/mol [Strepikheev et al. and eq. (11)]. The difference between -5.7 and -4.4 can be explained by a couple of factors. One, after our parameter estimation, the enthalpy of polycondensation had an estimated standard deviation of 0.6 kcal/mol. Two, the polymerization data were from polymerizations roughly 200°C higher than the

standard state for the combustion data. Small differences in relative heat capacities and the experimental errors from subtracting two large experimental numbers could easily explain the small deviation. Thus, the developed model is consistent with other nonpolyamidation results in the literature.

DEVELOPMENT OF MODEL—KINETICS

As indicated in the introduction, the kinetic rate constants also vary dramatically with water concentration. As an example, Ogata's[2] data show that not only does the equilibrium constant vary with water concentration but that the variation of the kinetic constant (about a factor of 7) is even larger than that of the equilibrium constant (about a factor of 3). These rate constants assumed second-order kinetics; the variation for third-order constants would be even larger. This means that a mechanism must be operating in addition to the one that is causing the variation of the equilibrium constant. Thus, in this section, a model will be developed that is not only consistent with the equilibrium model above, but also describes the observed kinetic variations.

To model nylon polymerization kinetics, some assumptions will be made. First, based on Wiloth's experiments with caprolactam hydrolysis[22,26] (Fig. 6), without any added acid catalyst, the conversion of caprolactam is very slow. In fact, the reaction rate appears to autoaccelerate (the more that is reacted, the faster the reaction). By contrast, an added acid gives immediate and rapid reaction. Normally, polycondensation kinetics assumes a mixture of uncatalyzed and catalyzed reaction. The kinetic model presented here will assume instead that all reaction is acid catalyzed
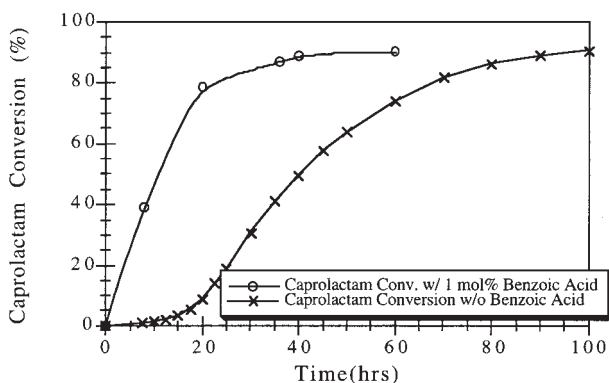

Figure 6 Effect of added acid on caprolactam conversion (Wiloth[22,26]).
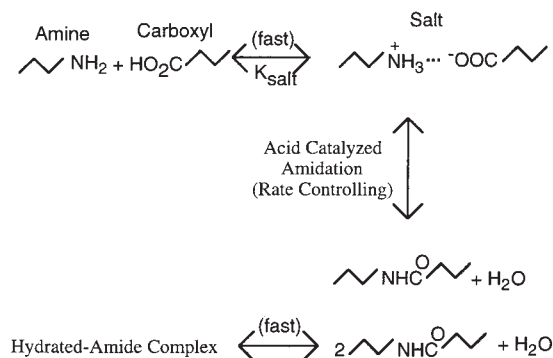
Figure 7   Proposed nylon polymerization mechanism consistent with observed kinetics and equilibrium data.

since conversion rates at time zero in Figure 6 seem vanishingly small. Such an assumption carries an added complication, however. If a reactor charge is assumed to be absolutely pure caprolactam with no added catalyst, then the model sketched out above implies no reaction would occur. Instead, the model will assume that all "pure" caprolactam contains a small amount of acid (6-aminocaproic acid, dissolved CO_2, some molecule associated with the wall, etc.). The user must specify this quantity; some typical numbers are shown at the end (Table II).

Normally, in the study of polycondensation reactions, the catalyzed reaction is associated with third-order kinetics. The proposed model then assumes that the reaction is first order with respect to each reacting end group. Thus, the overall reaction is first order with respect to amine concentration and second order with respect to carboxyl concentration.

Next, an overall nylon polymerization reaction mechanism will be proposed that is consistent with observed kinetic and equilibrium data. The first step is similar to the salting reaction (Fig. 7). Some features should be pointed out. First, due to the equilibrium reaction at the bottom of Figure 7, the equilibrium expressions developed earlier are conserved. Second, the mechanism has a prereaction equilibrium (the salting-like reaction); this will be crucial in causing water to affect reaction rates. Because the salting reaction is well known in the initial stages of nylon polymerization, this mechanism adopts a similar idea for higher conversions as well. For a very large value of the equilibrium constant K_{salt}, the mechanism in Figure 7 can explain the claim that nylon polymerization is second order at low conversions and switches to third order at higher conversions. In our model, we will assume that the majority of the reactive end groups are in the form of free

acid and amine; otherwise, additional constants would be needed to explicitly account for the salting reaction. For the second reaction in Figure 7, the basic forward rate is $k_f[\text{Salt}][\text{Acid Cat.}]$. while the first reaction equilibrium can be written as

$$K_{salt} = \frac{[\text{Salt}]}{[\text{Amine}][\text{Carboxyl}]} \qquad (12)$$

Thus, the overall rate expression for polycondensation becomes

$$k_f K_{salt}[\text{Acid Cat.}][\text{Amine}][\text{Carboxyl}] \quad (13)$$

This is a third-order expression that will be affected by the dielectric constant of the medium.

Morawetz and Otaki[27] proposed that all of the of the reactants for amidation should be in the zwitterion arrangement, i.e., that RCO_2^- and $R'NH_3^+$ are more stable than RCO_2H and $R'NH_2$. However, because the dielectric constants for polymer melts are very low, the work of Roses[28] implies that the zwitterion arrangement may not be the stable form for nylons at melt conditions; as dielectric constants are changed, the dissociation constants vary dramatically. Roses found the pKa of picric acid in water was 0.33 compared to 11.84 for picric acid in tetrahydrofuran. Here the dielectric constant changed from 78 to 7.5, and the dissociation constant by more than 11 orders of magnitude. The obvious way to understand this shift is that a high dielectric constant provides shielding for separated charges. As the dielectric constant is lowered, the shielding decreases and unlike charges associate again. For the case of the zwitterion arrangement, the carboxyl end should be affected in a fashion similar to what happens to picric acid. The amine (RNH_3^+) pKa, on the other hand, should be virtually unchanged because this dissociation does not involve charge separation. This means that the dissociation pKas in water (5 for acid and 11 for amine) should shift to 16 and higher for acid and 11 for amine in the nylon melt. In other words, the low dielectric constants of nylon melts (about 4) seem likely to destabilize the zwitterion arrangement.

Furthermore, the data of Heikens et al.[29] show that end group imbalances do not affect the polycondensation equilibrium. Because any excess reactant is unable to shift to the zwitterion arrangement, all excess has to be nonionized. This means that ionized and nonionized groups would exist simultaneously, but the work of Heikens et al.
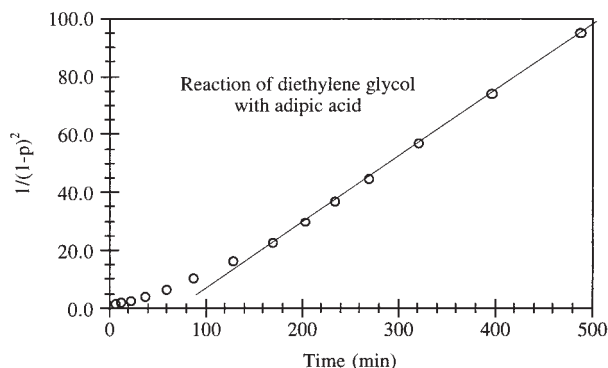
Figure 8 Polyesterification, third-order fit, data of Flory.[4]

shows that all end groups have the same activity. Therefore, the nonionized reactants would have to have the same activity as the ionized ones— difficult to believe. By contrast, if reacting groups are not in the zwitterion arrangement, this difficulty vanishes. Such a consistency gives more weight to the proposed scheme in Figure 7 and discredits the zwitterion scheme.

The reference in eq. (13) to acid refers to any acid, carboxyl or otherwise. Experiments with acids other than carboxylic acids are difficult to find. Flory's data for polyesterification[4] can be interpreted to show that the catalytic activity of an added acid varies linearly between the square root of the dissociation constant and the constant itself. Assuming that polyamidation and polyesterification are analogous, this means that a small amount of HCl or other strong acid will dramatically increase the reaction rate of nylons. However, such an effect is of little use industrially because an added catalyst increases the depolymerization rate as well, decreasing the stability of the final product.

The final required piece of the conceptual model is an effect that would cause the water concentration to affect the polymerization rate. Flory[4] theorized that the deviation from third-order kinetics early in the reaction (Fig. 8) is caused by a change in the dielectric constant. If a charge transfer prereaction equilibrium step is part of the overall reaction mechanism, then changes in the dielectric constant will drive changes in this equilibrium "constant." As the relative amounts of material that can react shift, the observed reaction rate changes. Born[30] showed that changes in the dielectric constant of the medium affect the interaction energy of charged species ($\Delta U = C \Delta (1/\varepsilon_r)$). With a Boltzmann partitioning, the equilibrium

constant (for the "salting" prereaction equilibrium step) will vary as $\exp(-\Delta U/RT)$.[31] These changes, in turn, will affect the quantity of reactants that are able to react, affecting the observed reaction rate.

For the reaction scheme of Figure 7, the effect of water on the reaction rates can be understood easily. Water, due to its high polarity, greatly affects the dielectric constant. A higher dielectric constant stabilizes the left-hand side of the "salting" reaction, reducing the amount of material that can participate in the rate-controlling step. Mathematically, K_{salt} is proportional to $\exp(-\Delta U/RT)$. As the water content increases, K_{salt} decreases due to the changing dielectric constant. The reduced K_{salt} then reduces the apparent rate [eq. (13)].

Flory's[4] article on polyesterification makes the dielectric constant idea more plausible than the standard assumption of varied kinetic order. Flory observed the conversion to deviate from the third-order behavior only at short times (see Fig. 8). This is when the dielectric constant is expected to change the most. Furthermore, the deviation is such that reaction is slower than the third-order kinetics would predict. This, too, is just what is expected because the dielectric constant is largest here. By contrast, with a mixed-order reaction rate, if the third-order part is dominant over the second-order part at high conversions, then the third-order part should be dominant over the whole range of conversions; Flory's data do not show this. Thus, a dielectric effect is both plausible and consistent with the data trends for polyesterification and, by implication, for polyamidation also.

In summary, by combining these effects, the forward rate constant for polycondensation, ring closing, and polyaddition was calculated as

$$k_{f,i}(T, \varepsilon) = k_{0,f,i} \ (T = 230°C)$$

$$\exp\left(-\frac{E_{a,i}}{R}\left(\frac{1}{T} - \frac{1}{503.15}\right)\right)\exp\left(\frac{C}{\varepsilon RT}\right) \quad (14)$$

Ring closing is calculated instead of ring opening because then polycondensation and ring closing both represent creation of an amide linkage; this makes the parameters more comparable. Equation (14) was used to calculate the rate constant for polycondensation ($k_{f,1}$), ring closing ($k_{f,2}$), and polyaddition ($k_{f,3}$) (reactions 15, 16, 17) for nylon 6 and 66.

$$R_{\text{Polycondensation}} = k_{f,1}[\text{Acid}]^2[\text{Amine}]$$

$$- \frac{k_{f,1}}{K''}[\text{Acid}]w_f(\lambda_1 - \lambda_0) \quad (15)$$

$$R_{\text{Ring closing}} = k_{f,2}[P_1] - \frac{k_{f,2}}{K_2}[\text{CL}]w_f \quad (16)$$

$$R_{\text{Polyaddition}} = k_{f,3}[\text{Amine}][\text{CL}]$$

$$- \frac{k_{f,3}}{K_{\text{add}}}[\text{Amine}^{2+}] \quad (17)$$

In reaction 15, λ_0 and λ_1 represent the zeroth and first polymer moments (for more discussion consult Jacobsen and Ray[14]). The difference, $\lambda_1 - \lambda_0$, represents the concentration of polymer linkages that the condensate molecule can attack.

For each reaction (polycondensation, ring closing, and polyaddition), $k_{f,i}$ and $E_{a,i}$ were estimated. Only one value of C was found for all three reactions with the same equilibrium constants found earlier. Finally, the constant A_e for the polymer dielectric constant (see below) was also estimated. This amounts to a total of eight constants.

Other Physical Data Needed for Modeling

Accurate numbers for high-temperature nylon dielectric constants are difficult to find. Here, a decaying exponential expression was used

$$\varepsilon_{\text{polymer}} = 1 + A_e\exp(4041/RT) \quad (18)$$

This expression fits low molecular weight amide data at high temperatures and forces the dielectric constant to be greater than 1. The exponential constant (4041 cal/mol/°C) was determined based on published dielectric data[32] for N-(1-butyl)acetamide—similar to the monomer. The parameter A_e was estimated as part of the overall parameter estimation and assumed to be the same for monomer, polymer, and rings. This step was also necessary because polymers have dielectric spectra that are frequency dependent at diffusion/relaxation time scales of the system, while the water molecule, being much smaller, can adjust more quickly. Particularly, if the "salting" step time scale is fast compared to the relaxation time scale of the polymer, a static dielectric constant would not be appropriate.

To model the change in reaction rate with dielectric constant, a mixing rule for dielectric constants is needed to predict what happens as composition varies. As a first step, the constants were assumed to add according to each component's weight fraction. Examination of experimental evidence[32] from water-amide solutions shows this to be somewhat incorrect; an approximately 50–50 (by weight) solution of water/N-(1-butyl)acetamide has a dielectric constant of about 69, which is below 78 for pure water and 100 for pure N-(1-butyl)acetamide. This problem was partly resolved by Kurosaki's work,[23] referred to earlier (Fig. 5). Kurosaki's results for silica gels can be extended to nylons by assuming that the water in the "water bridge" state is tightly sorbed, giving the dielectric constant of ice. Next, water merely sorbed to the polymer has half the dielectric constant of pure water. As mentioned earlier, because two states for water were considered, this "free water" concentration was assumed to be that of the water not in a "water bridge." In other words, the dielectric constant was calculated through an expansion around the zero water concentration point. This analysis makes the same assumption as made in the equilibrium discussion: two states instead of three for water. Furthermore, water is assumed not to affect the apparent polymer dielectric constant. Specifically, the overall dielectric constant may be expressed as

$$\varepsilon = \varepsilon_{\text{ice}}(\omega_{w,\text{tot}} - \omega_{w,f}) + 0.5\varepsilon_{\text{water}}\omega_{w,f}$$

$$+ \varepsilon_{\text{polymer}}(1 - \omega_{w,\text{tot}}) \quad (19)$$

In eq. (19), $\omega_{w,\text{tot}}$ refers to the mass fraction of total water and $\omega_{w,f}$ refers to the mass fraction of free water.

In both equilibrium and kinetic models, concentrations should be expressed in mol/L, not per kilogram.[6] This variation is important because a set of equilibrium and kinetic expressions is desired that describe mixtures that differ by as much as 10% in density. A 10% density difference translates to a 21% difference in conversion rates for third-order kinetics. For nylon 6, the density relationship in Giori and Hayes' article[6] was used with the constant term adjusted to 1.10 to agree with the data in the *Polymer Handbook*.[33] A similar adjustment was used for nylon 66 and 7.

$$\rho_{\text{polymer}} = \begin{cases} 1.10 \text{ for nylon} \\ 1.129 \text{ for nylon 66 or 7} \end{cases}$$

$$-0.00052(T - 273.15) \quad (20)$$

Equation (20) gives the density in kg/L. The caprolactam density was calculated as 0.91 of the nylon 6 density.[34] The monomer (6-aminocaproic acid, HMDA, or adipic acid) densities were as-

sumed to be the same as the polymer. This probably does not entail a large error because the concentrations are either small or are rapidly consumed. Water densities and dielectric constants were taken from the *Handbook of Chemistry and Physics*.[35] Reacting mixtures were assumed to be incompressible, and no density corrections were made for reactor pressure. Finally, the mixture density was based on an ideal mixing rule where the specific volumes are assumed to be additive according to each component's mass fraction [eq. (21)].

$$\frac{1}{\rho_{\text{overall}}} = \sum_{\text{components}} \frac{w_i}{\rho_i} \qquad (21)$$

RESULTS OF MODEL—KINETICS

Previously the equilibrium model was compared to a wide range of data, including some that were not even used for estimating the parameters. In this section, a similar study will be done to compare the model to kinetic data.

Parameter Estimation

The data used for the kinetic parameter estimation were polymerizations at 200–220°C of nylon 66 salt with initial water contents between 3.5 wt % and 40.7 wt %,[2] polymerizations of caprolactam at 220°C with initial water contents between 0.15 wt % and 0.6 wt %,[22] polymerization of caprolactam at 235, 245, 255, and 265°C with an initial water content of 2 wt %,[6] nylon 7 hydrolysis,[6] and caprolactam polymerization experiments between 230 and 270°C with initial water contents between 0.75 to 2.1 wt %.[8] Values for the end group concentrations (and caprolactam concentrations where appropriate) were used as data for fitting the model in a weighted least-squares sense. Weights for individual points were calculated so that the model minimized the relative errors not the absolute errors; this change was necessary to ensure that the parameter estimation did not ignore some small (but significant) end group concentration data and only predict the caprolactam conversion data, which were often about three orders of magnitude larger. Values of estimated kinetic and equilibrium constants are summarized in Table II. As mentioned earlier, polymerization of neat caprolactam requires an initial acid concentration. Three initial monomer concentrations for the three different authors' nylon 6 polymer-
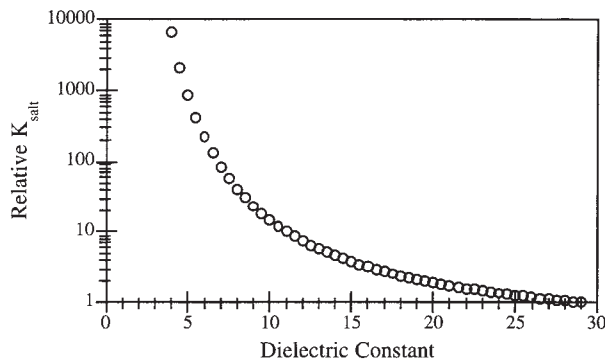

Figure 9 Effect of dielectric constant on salting reaction.

izations were also found. The same numerical values for the parameters were used for all polymerization systems (nylon 66, nylon 6, and nylon 7).

Examination of Estimated Constants

The only way to check many of the constants associated with the kinetics of nylon polymerization is to compare them against experimental data. However, two of the constants fitted in the model relate to more general aspects of nylons and can be checked externally. First, the dielectric constant preexponential factor. This constant predicts a dielectric constant in dry nylon of 4.8 at 230°C. Examination of *Polymer Handbook*[33] data makes this value seem plausible.

The coupling of the dielectric constant to reaction rate relates to some polyamide steady-state phenomena as well. Because

$$K_{\text{salt}} \propto \exp\left(\frac{C}{\varepsilon RT}\right)$$

the variation of this salting-like reaction with the dielectric constant can be determined. Figure 9 shows the relative values of K_{salt} normalized with the value for pure water—all numbers for 230°C. These large variations in K_{salt} are what drive changes in the reaction rate as the water content changes. Earlier, the likelihood of the zwitterion arrangement in concentrated nylon melts was examined. There, the work of Roses[28] was introduced to show how, when the dielectric constant changes, the relative dissociation constants can also vary by orders of magnitude (as in Fig. 9). Numerically, a constant C can be calculated from the relative picric acid dissociation constants
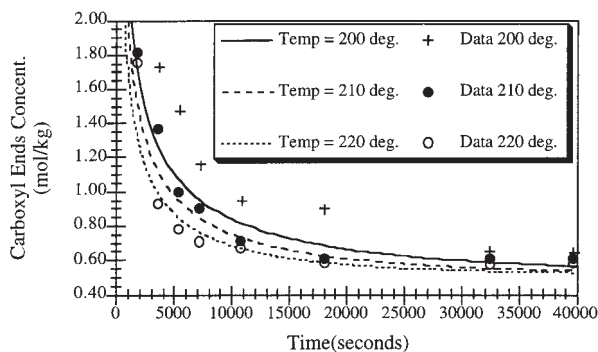
Figure 10   Effect of temperature on nylon 66 polymerization, data of Ogata,[2] initial water content 30 wt %.

$$\left(K_a \propto \exp\left(\frac{C}{\varepsilon RT}\right)\right): \quad 33,470 \text{ cal/mol}$$

Although the exact nature of the "salting-like" reaction is not the same as acid dissociation, one would expect the constant C to be on the same order of magnitude for the two cases. Our estimated value of C was found to be 40716 cal/mol (see Table II). In other words, the constant for the dielectric effect seems consistent with literature dissociation data.

Low-Temperature Nylon 66 Polyamidation

Relatively low temperature and high water content polymerization of nylon 66 is interesting because this represents one of the early stages of nylon polymerization. Figures 10 and 11 show how the model predicts nylon 66 polymerization as the temperature and water content are varied, respectively. The deviation in the 200°C data may be due to slow melting and dissolution of the nylon salt at the low temperature; highly crystalline monomers are known to undergo only very slow polymerization in the solid state.[36] Because very
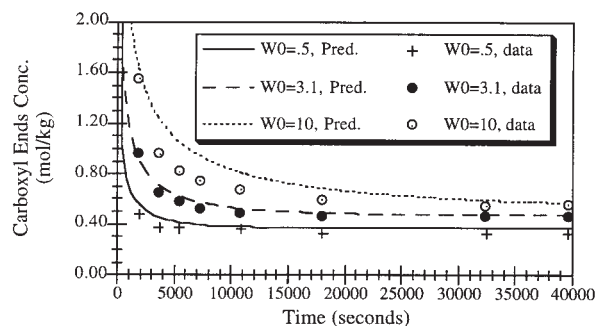

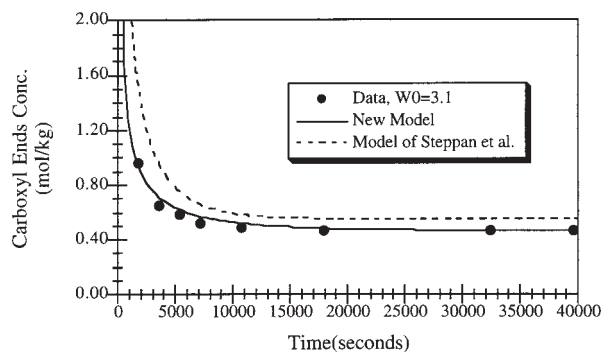**Figure 11**   Effect of water on nylon 66 polymerization, data of Ogata.[2]

Figure 12   Comparison of new model, model of Steppan et al.,[5] and data of Ogata[2] at 220°C.

little data is available for nylon 66 cyclization reactions (the dimer can cyclize), no cyclization reactions were included in the model, except for the formation of caprolactam (nylon 6 only). The conversion underprediction for the highest water content in Figure 11 may be due to the unmodeled cyclization reactions. As higher water concentrations are approached, previously negligible cyclization reactions become more important because intramolecular reactions are not slowed by dilution as intermolecular ones are. Ogata used W0 to refer to the initial mol ratio of water to monomer (mol of H_2O/mol of HMDA or adipic acid); this designation is preserved in Figures 10, 11, and 12.

Comparison of Nylon 66 Models

Also of interest in this study is how the new model compares to the empirical model of Steppan et al.[5] As mentioned in the introduction, Steppan and co-workers did an extensive data correlation on nylon 6 and 66 data. Figure 12 shows the comparison against Ogata's data; the proposed model is somewhat better but both are very reasonable representations.

Nylon 6

Not only is the production of nylon 6 another important industrial process, but nylon 6 is also an important test system for both nylon 6 and 66. Experiments at high temperatures have the disadvantage of simultaneous degradation during the polymerization; however, because nylon 6 melts at lower temperatures than nylon 66 (220 vs. 255°C), nylon 6 can be studied at melt conditions at relatively low temperatures. Because nylon 6 polymerizations have a largely ring chain addition character (not polycondensation), these
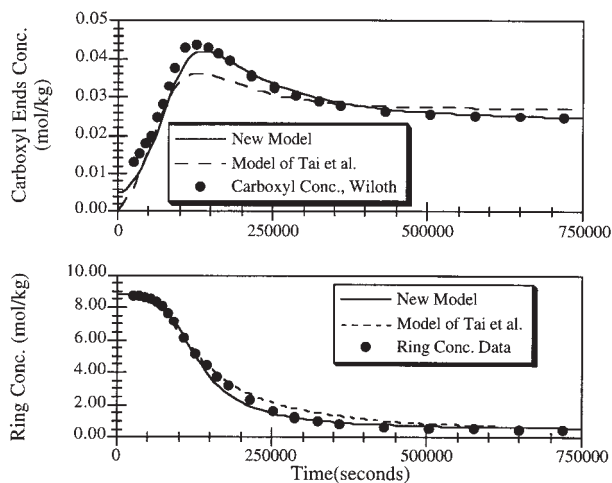
Figure 13 Polymerization of 220°C with 1 mol % (data of Wiloth[22]).

polymerizations are natural for easily exploring the effects of low water content, allowing one to start out with a low water content (no mass transfer is required). Thus, by experimenting with nylon 6, polymerization at low water contents and temperatures can be studied and understood, while the complicating effects of degradation reactions are avoided.

Nylon 6 at Low Water Content and Low Temperatures

Wiloth[22] has carried out nylon 6 reactions with low water contents leading to molecular weights of as high as 35,000. Such molecular weights are industrially germane, and so any proposed model should handle them. Figures 13 and 14 compare the proposed model, the model of Tai et al., and
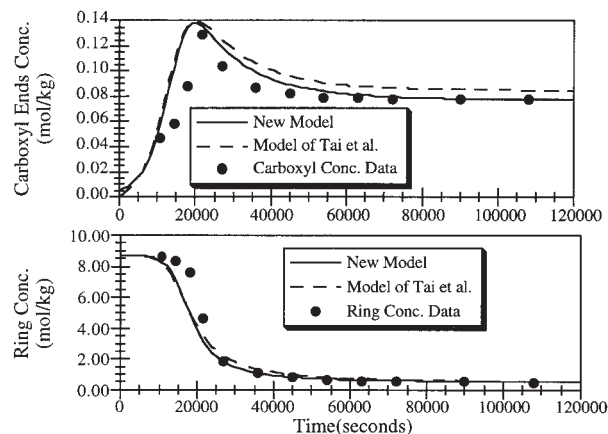

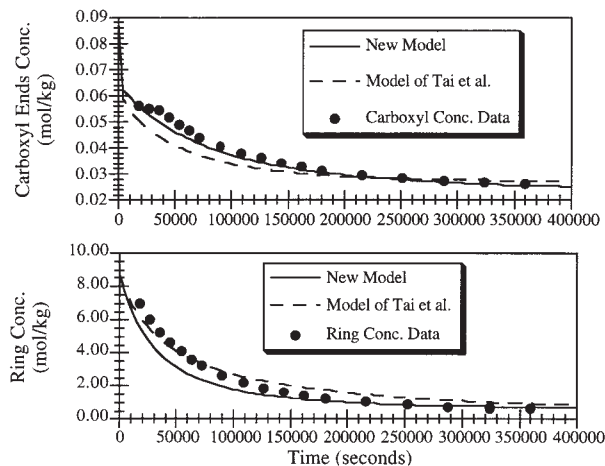**Figure 14** Polymerization at 220°C with 8 mol % water (data of Wiloth[22]).

Figure 15 Polymerization at 220°C with prehydrolyzed caprolactam (1 mol %) (data of Wiloth[22]).

Wiloth's data at 220°C for two different water concentrations: 1 and 8 mol %. The model (Table I) of Tai et al.[9] is the standard model that assumes constant equilibrium (all data fits are done at very low water contents) and a mixture of second- and third-order reaction for all the reactions of Figure 1. All of the nylon 6 data fits will be compared to this model as well. Both models follow the data reasonably well, with the proposed model doing somewhat better in both cases.

Examining qualitatively different data can determine a model's comprehensiveness. In Figure 15, Wiloth's experiment of starting with prehydrolyzed caprolactam is analyzed. Here, instead of using neat caprolactam mixed with water, the water portion was used to preopen caprolactam rings. This means that the 1 mol % of water was used to create a starting mixture of 99% caprolactam and 1% 6-aminocaproic acid. The models differ somewhat. Because the model of Tai et al. underpredicts the end group concentration, the ring conversion (being mostly acid catalyzed) is less than would have otherwise occurred with the correct endgroup concentration. In other words, the proposed model predicts the end group concentration slightly better, and the difference in ring conversion predictions is not very meaningful.

Nylon 6 at Higher Temperatures

The ability of the model to handle a variety of temperatures is also important. The comparisons of Figure 16 represent a best-case scenario for the model of Tai et al. because the data shown were used to determine the constants in the model of Tai et al. These conditions are also interesting
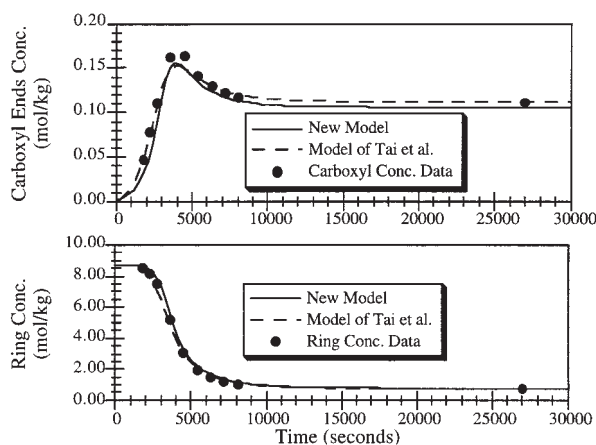
Figure 16   Nylon 6 polymerization at 259°C and 1.5 wt % water (Tai et al.[8]).

because of the higher temperature. Figure 16 shows both models compared to the data. Performance is very similar.

A Priori Prediction of Nylon 6 Data

Because a model is expected to follow the fitted data, comparing the model against other data is a good testing method. In Figure 17, the proposed model and the model of Tai et al. are compared against the data of Hermans et al.[37] For applying the proposed model, the initial monomer concentration was assumed to be 0.003 mol/kg. This is roughly the mean value of the estimated parameters summarized in Table II. These values should vary as experimental procedures are varied. The data and both models compare well.
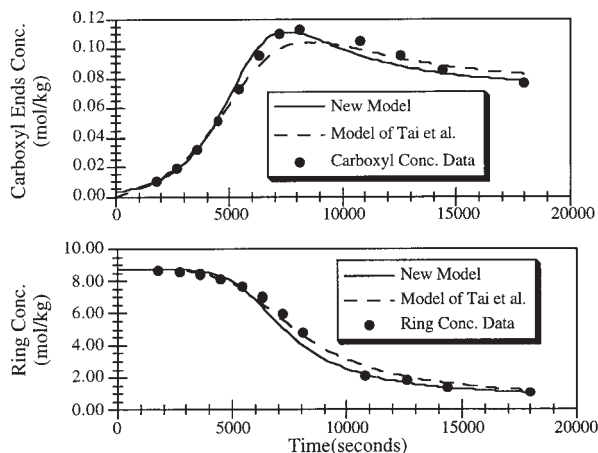

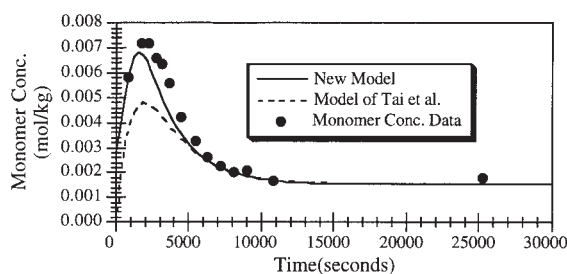**Figure 17**   Melt polymerization of nylon 6 compared to data of Hermans et al.[37] at 253.5°C.

Figure 18   Monomer concentration during the polymerization of nylon 6 at 259°C and 0.82 mol/kg of water (data of Tai et al.[8]).

A Priori Prediction of Monomer Concentration

Another interesting aspect of the model is the monomer concentration (6-aminocaproic acid) in nylon 6 melts. This concentration is used as an explicit state in nylon 6 models where polymer moments are calculated because the ring opening reaction plays such an important part. Because Tai et al.[9] determined the caprolactam, end group, and monomer concentrations, both models (Tai et al. and this work) can be compared. These are true model predictions because no monomer data were used to fit either model. Figure 18 shows the improvement the proposed model gives to *a priori* predictions of monomer (6-aminocaproic acid) concentration.

Earlier, parameter estimation required the assumption of an initial monomer concentration. Because the improvement in matching the peak in Figure 18 is about the same as this initial amount, one might suspect that the assumption of an initial monomer concentration has caused the improvement. This is not the case. If an initial monomer concentration is used that is 0.1 of the value used to generate the "new model" curve in Figure 18, the peak height is almost identical. The only change is the time that the peak occurs, which is expected for an autocatalytic reaction. Thus, the proposed model also predicts the monomer concentration without any further parameter estimation. This gives additional credence to the proposed model.

Performance of the Model with Unbalanced End Groups

The data considered in this article to this point have been only for those with end groups (amine and carboxyl) that are balanced. For completeness, the implications for unbalanced ends will be studied. Earlier the effect of acid strength was discussed, particularly that strong acids are much
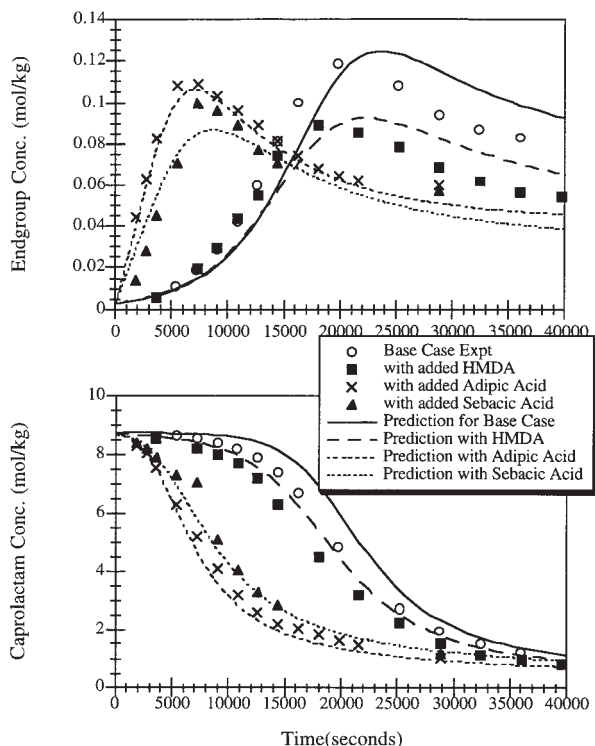
Figure 19 Model prediction of nylon 6 melt polymerization with end group imbalances (data of Heikens et al.[29]).

better catalysts. Now, the effect of RCO_2H or $R'NH_2$ in excess will be investigated, i.e., the amounts are varied not the reactivities. The mechanism of Figure 7 is first order in acid, first order in carboxyl concentration, and first order in amine concentration. For carboxylic acids of approximately the same dissociation constant as the carboxyl end of nylon 6, the kinetic order reduces to first order in amine concentration and second order in carboxylic acid concentration. The data of Heikens et al.[29] are consistent with these reaction orders (shown in Fig. 19).

Here, four different experiments at 221.5°C are compared to the model predictions. The first experiment is a plain polymerization with pure caprolactam. The second adds 0.4 wt % HMDA (hexamethylene diamine). The next adds 0.6 wt % adipic acid, and the fourth 0.8 wt % sebacic acid. The assumed initial acid (hydrolyzed caprolactam) was assumed to be 0.003 mol/kg, just as above. Two points are apparent. First, the polymerizations with the added acid are better described. This is to be expected because then small changes in the assumed initial acid content do not have a large effect on the reaction rate. More particularly, however, the model quantitatively predicts the effect of imbalances in the various

endgroup concentrations. This confirms the expected effects discussed earlier.

A Note on Initial Monomer Concentration

Table II shows the difference in the fitted initial monomer concentration for various authors' nylon 6 data. Although these numbers are roughly similar, the difference might be attributed to more than just apparently minor variations in caprolactam purification, gas evacuation, or other experimental details. For example, the experiments of Wiloth were at a lower temperature than the average for those of Tai et al. Is the higher (fitted) initial monomer content related to the lower temperature? Particularly, the data of Tai et al.[8] were examined by using the overall experimental constants and looking at the initial monomer concentration that gave the best fit for each individual polymerization run. The estimated initial monomer concentrations showed no clear trends, and varied by as much as a factor of 2. This variation implies a limit to the accuracy any parameter estimation could achieve.

Implications for Interchange Reactions

Controlled blending of polycondensation polymers allows access to block copolymers. These polymers, like free radically produced copolymers, can have special properties not seen in either of the homopolymers. However, unlike free radical mechanisms, mixtures of condensation polymers, if left at reaction temperature long enough, will be merely random copolymers.

The kinetic scheme discussed can be used to validate the amide interchange rate constants of Miller.[38] Because water can affect interchange rates so strongly, an external estimate of the reaction rates is useful to make sure that any observed interchange is not merely hydrolysis followed by the forward reaction. Hermans et al. theorized that the following rate relation holds:

$$\frac{\text{transamidation}}{\text{polyaddition}} = \frac{\text{hydrolysis of chain amides}}{\text{hydrolysis of lactam}} \quad (22)$$

This means that the amine group is hypothesized to attack the two types of amides (nylon linkages and caprolactam) in the same ratio as water does. If the difference in rates is due mostly to ring strain and relative accessibility, this hypothesis

seems reasonable, leading to a rate constant for transamidation in dry nylon of 6.0 kg^2/mol^2/h at 230°C (from the constants in Table II). By contrast Miller's work gives rates of 3.0 kg^2/mol^2/h at 231°C and 7.2 kg^2/mol^2/h at 275°C. (The same calculation done with the rate constants of Tai et al. gives a value of 2.1 kg^2/mol^2/h at 230°C). Because the primary difficulty when determining interchange rate constants is the reservation that reverse polycondensation followed by forward polycondensation might account for the interchange, observing experimental numbers about the same or somewhat less than the prediction is not worrisome. Furthermore, the estimates of the transamidation rate constants were made by an analogy that is basically qualitative; exact values of the constants cannot be expected. In conclusion, the transamidation rate constants of Miller (the carboxyl catalyzed attack of an amine on an amide linkage) seem correct, and the assumed mechanism is consistent with kinetic constants derived for nylon 6 systems. This is another example of the value of combining nylon 6 and 66 data sets to gain a better understanding of the system.

Implications for Ring Oligomers

Another area of interest in nylon systems is the concentration of ring oligomers. Ring oligomers, unlike other low molecular weight species such as monomer and dimer, reach a limiting value that is virtually independent of conversion. This interesting situation can be seen from the equilibrium relation for the polyaddition of dimer (reaction 5 of Fig. 1).

$$K = \frac{[-NH_2^{3+}]}{[R_2][-NH_2]} \qquad (23)$$

The "3+" on the product end concentration means that only those polymer chains with three or more repeat units in the chain are included. At low conversions, some ends (such as an opened ring) are unable to participate in the reverse reaction. By contrast, at high conversions, the fraction of low molecular weight material approaches zero. The end group concentrations in the equilibrium expression [eq. (23)] cancel, and the equilibrium constant varies merely as the inverse of the ring concentration. This means that changes in operating conditions can not reduce ring oligomer content except kinetically. In fact, to reduce the concentration of these species, nylon 6 is often washed. This means then that kinetic modeling can be useful to predict the extent of ring oligomers.

Examination of kinetic rates for the formation of caprolactam (Table II) shows that reverse polyaddition produces caprolactam about 20 times faster than ring closing at a degree of polymerization of 100. Furthermore, approximate analysis of the dimer ring production rates[12] shows these rates to be second order in end group concentration. This is consistent with reverse polyaddition being the dominant formation route, not ring closing. Ring closing should be third order with respect to end group concentrations (acid catalyst and dimer concentration from a most probable distribution), and reverse polyaddition is second order. Therefore, reverse polyaddition was assumed to be the only reaction responsible for formation of ring oligomers (reaction 5 of Fig. 1). Next, the enthalpy of reaction was fixed at zero. This is consistent with ring strain data for cycloalkanes[39]; 14 membered rings have no appreciable strain. Two equations define the production of dimers [eqs. (24) and (25)].

$$\frac{d[R_2]}{dt} = k_{\text{dimer}}[\text{Acid}][R_2][\text{Amine}]$$

$$- \frac{k_{\text{dimer}}}{K_{\text{add,dimer}}}[\text{Acid}][\text{Amine}^{3+}] \quad (24)$$

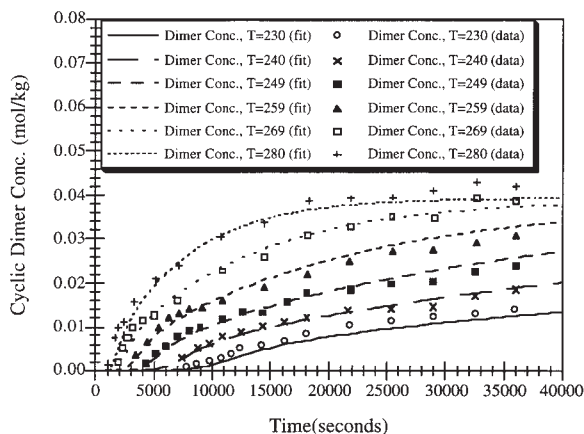$$K_{\text{add,dimer}} = \exp\left(\frac{\Delta S_{\text{add,dimer}}}{R}\right) \qquad (25)$$

Like the other reactions, the kinetic expression (for k_{dimer}) was assumed to vary with water content as in eq. (14). The data of Arai et al.[12] were then used to estimate this three constant model: rate at 230°C, activation energy, and entropy of reaction (constants are listed in Table III). The overall agreement with the data is quite reasonable; Figure 20 shows the comparison between data and model with a water content of 0.82 mol/kg. (The same parameters also model well the data at water contents of 0.42 and 1.18 mol/kg.) This new model is of the same basic quality as that of Arai et al. except this section of the nylon model has 3 fitted parameters, not 12. Furthermore, because ring closing is not included, the model is thermodynamically consistent.

At this point a simple *a priori* theory for higher (three and more monomer unit) ring oligomers can also be constructed. The reaction is essentially reaction 5 of Figure 1 with *n*mer in place of dimer. Here, the enthalpy of reaction is as-

Table III   Cyclic Dimer and Higher Cyclic Oligomer Parameters

Fitted Cyclic Dimer Parameters	
Rate of polyaddition of dimer rings at 230°C	9.7×10^{-4} L^2/mol^2/h
Activation energy for polyaddition of dimer rings	10,530 cal/mol
Entropy of dimer ring polyaddition reaction	6.495 cal/mol/°C

Assumed Cyclic Dimer Parameters	
Enthapy of dimer addition	0.0 cal/mol

Higher Oligomers Reaction Entropies	
Entropy for trimer ring polyaddition	8.509 cal/mol/°C
Entropy for tetramer ring polyaddition	9.939 cal/mol/°C
Entropy for pentamer ring polyaddition	11.047 cal/mol/°C
Entropy for hexamer ring polyaddition	11.953 cal/mol/°C

sumed to be the same as the dimer (i.e., zero). The entropy of reaction can be calculated by using the Jacobson and Stockmayer theory,[40] predicting the ring cyclization equilibrium constant to vary as $n^{2.5}$. Next, the activation energy for polyaddition of $n$mer is assumed to be the same as for the dimer reaction (the same bonds are being broken). Finally, because a dimer has two attack points and an $n$mer has n, the forward reaction rate constant (consumption of $n$mer) is just $(n/2)k_2$. The kinetics and equilibrium are then expressed in eqs. (26) and (27).

Figure 20   Fit of nylon 6 cyclic dimer data (Arai et al.[12]) (water = 0.82 mol/kg).

$$\frac{d[R_n]}{dt} = \frac{n}{2} k_{\text{dimer}} \left\{ [\text{Acid}][R_n][\text{Amine}] \right.$$

$$\left. - \frac{1}{K_{\text{add},n\text{mer}}} [\text{Acid}][\text{Amine}^{(n+1)+}] \right\} \quad (26)$$

$$K_{\text{add},n\text{mer}} = \left(\frac{n}{2} \right)^{2.5} K_{\text{add,dimer}} \quad (27)$$

The designation amine$^{(n+1)+}$ is similar to that in eqs. (9) and (23); only chains with at least $n+1$ monomer units can undergo reverse polyaddition to produce a ring $n$mer.

There seem to be no usable kinetic data in the literature. However, equilibrium contents however are available; Table IV compares the collected equilibrium values of Tai and Tagawa[11] to those calculated by the above theory. Given the scatter in the published data, the model proposed seems adequate to describe the polymerization system. Because the reaction enthalpy is assumed to be zero, changing the temperature does not affect the ring concentrations. Calculated entropies of reaction for the higher rings are listed in Table III [using eq. (25) instead of (27) to calculate $K_{\text{add},n\text{mer}}$).

The quality of the model shown in Table IV compared to earlier models is related to the assumptions used. Andrews et al.[43] attempted to use the Jacobson theory (and got poor results) by starting with the equilibrium constant for caprolactam. Because this reaction has a nonzero enthalpy (reaction 3 of Table I), one expects considerable changes from caprolactam to the higher ring oligomers. By contrast, in this work, the enthalpy of dimer ring polyaddition was assumed to be zero, and the dimer equilibrium constant was used as a starting point.

A fit of Tai and Tagawa's equilibrium[11] concentrations for varying water content and temperature could also be attempted in addition to the comparisons in Table IV. However, the experimental reaction time used to determine these concentrations (10 h) is unlikely to lead to equilibrium, especially at the lower temperatures. Just because properties such as end group and caprolactam concentration are stationary does not mean the higher cyclic oligomer concentrations are. For example, at the lowest water content and the highest temperature (0.42 mol/kg and 280°C), Tai et al.[9] show the caprolactam concentration to be at equilibrium in about 4 h. By contrast, the cyclic dimer concentration takes about

Table IV   Ring Oligomer Concentrations in Nylon 6 Melts

Origin	Temp. (°C)	Water (mol/kg)	Ring Oligomer Conc. (mmol/kg)			
			$[R_3]$	$[R_4]$	$[R_5]$	$[R_6]$
Mori and Takeuchi[41]	—	—	13.8	6.6	3.0	2.4
Mochizuki and Ito[42]	—	—	15.9	8.2	5.5	—
Tai and Tagawa[11]	259	0.82	14.3	6.9	2.2	0.9
This work (*a priori* model pred.)	259	—	13.8	6.7	3.9	2.4

10 h at these conditions to reach equilibrium. Because most of the other data is at lower temperatures, 10 h is too short to achieve equilibrium for the higher oligomer concentrations.

Tai and Tagawa also claimed that higher water contents led to higher equilibrium oligomer concentrations. Because these reactions are second order in end group concentration, the higher water content concentrations should increase faster. This effect alone could have caused the apparent variation seen by Tai and Tagawa, because, from a theoretical standpoint, small changes in the water content at high conversions should have no effect on the equilibrium ring concentration. In other words, the equilibrium effects claimed by Tai and Tagawa could be kinetic variations due to the long time required to achieve complete equilibrium.

CONCLUSIONS

A comprehensive model encompassing not only molecular weights and ring conversion but also interchange reactions and cyclic oligomer formation has been developed and tested against experimental data. The model has the unique quality of handling water concentration in a fundamental fashion with a minimum of fitted parameters and no empirical functional forms. Agreement between the data and the model in all cases is reasonably good and allows use of the model to calculate a variety of quantities of interest. Finally, the development of this model will allow further study of the complex kinetics of nylon solid-state polymerization and nylon reactors.

NOMENCLATURE

ACA	6-aminocaproic acid
A_e	preexponential factor in equation 18
A_s	concentration of carbonyls with a water bridge
A_{tot}	concentration of total carbonyls
A_u	concentration of carbonyls without a water bridge
C	dielectric effect constant [eq. (14)]
CL	caprolactam
C_s	concentration of carboxyls with a water bridge
C_u	concentration of carboxyls without a water bridge
E_a	activation energy
k_f	forward rate constant from Figure 7
k_2	forward rate of dimer polyaddition
K' and K''	defined in eq. (4)
K_{add}	equilibrium constant for the addition reaction
K_{salt}	equilibrium constant for the "fast" reaction in Figure 7
L	concentration of water bridges
P_1	monomer (6-aminocaproic acid) (same as ACA)
P_2	dimer (nonring)
P_s	concentration of amide linkages with a water bridge
P_u	concentration of amide linkages without a water bridge
R	universal gas constant
R_n	nylon 6 ring with n monomer units
$R_{reaction}$	rate of designated reaction
t	time
T	temperature (K)
w_f	concentration of water not in a water bridge
w_{tot}	total water concentration
ε	dielectric constant
λ_0	zeroth polymer moment
λ_1	first polymer moment
ρ	density (kg/L)
ω	mass fraction of a component

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