An Analysis of Caprolactam Polymerization

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A versatile model for classical polymerization is presented. A deterministic, mathematical basis for obtaining the most probable distribution of molecular weights in batch polymerization is developed. Continuous polycaproamide production has been modeled and shown to give other than most probable distribution in many cases. The effect of adding monofunctional agents has been investigated. Results of some preliminary studies toward determining the optimal reactor configuration are presented.

INTRODUCTION

Recent papers by Reimschussel and coworkers (1-4) have dealt with various aspects of nylon-6 production by hydrolytic polymerization of ε-caprolactam. Focusing on reaction conversion or number-average molecular weight as variables of interest, problems treated have been: condensation equilibrium in the presence of additives (1), polymerization in a CSTR and other series configurations (2), the minimum time optimization problem (3) and the re-equilibration of nylon-6 (4). It has been stated or assumed in all these treatments that a most probable distribution of polymer chain lengths describes the reaction product. For a product like nylon-6 that is typically processed by extrusion and melt spinning, molecular weight distribution, through its effect on melt viscosity, is a very important property. The most probable distribution of molecular weights is found in most commercial nylon-6 products (18) and does indeed give a desirable product of uniform quality (20).

With these factors in mind, we have developed a treatment of caprolactam polymerization which can predict not only conversion and number-average degree of polymerization, but also can describe mathematically the molecular weight distribution as a function of reaction time. Our objective has been to formulate a model adaptable enough to be applied to a wide variety of reactor conditions and configurations. We are able to show in which reactor designs a most probable distribution is indeed the expected product and how it may be drastically different in a CSTR or in other reactor configurations. In this same vein, the common practice of adding a monofunctional agent to control molecular weight is examined in some detail with regard to its effect on molecular weight and molecular weight distribution.

CHEMISTRY OF CAPROLACTAM POLYMERIZATION

There are two basic reaction schemes that are of commercial interest for the polymerization of ε-caprolactam.

The hydrolytic process (5) consists of the reactions illustrated in Table 1. There is an abundance of kinetic information available in the literature on this polymerization mechanism (6-10). From a chemical

<table>
<thead>
<tr>
<th>Table 1. Hydrolytic Polymerization</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initiation: ring opening</td>
</tr>
<tr>
<td>[ \text{HN-} \overset{(M)}{(\text{CH}_2)_5} \text{C}=\overset{(W)}{\text{O}} + \overset{(S_1)}{\text{H}_2\text{O}} \overset{k_1}{\Rightarrow} \overset{(M)}{\text{NH}_2-} \overset{(W)}{(\text{CH}_2)_5} \text{C} \overset{(S_1)}{\text{OH}} ]</td>
</tr>
<tr>
<td>Propagation: polycondensation</td>
</tr>
<tr>
<td>[ \overset{(S_n)}{\text{NH}<em>2} + \overset{(S_m)}{\text{HOOC}} \overset{k_2}{\Rightarrow} \overset{(S</em>{n+m})}{\text{CONH}} \overset{(W)}{\Rightarrow} \overset{k_2'}{\text{H}_2\text{O}} ]</td>
</tr>
<tr>
<td>polyaddition</td>
</tr>
<tr>
<td>[ \overset{(S_n)}{\text{NH}<em>2} + \overset{(M)}{\text{HN-}} \overset{(S</em>{n+m})}{(\text{CH}<em>2)<em>5} \text{C}=\overset{(W)}{\text{O}} \overset{k_3}{\Rightarrow} \overset{(S</em>{n+m})}{\text{NHCO}} \overset{(S</em>{n+1})}{(\text{CH}_2)_5} \text{NH}_2 ]</td>
</tr>
<tr>
<td>Reaction with monofunctional species:</td>
</tr>
<tr>
<td>[ \overset{(S_n)}{\text{NH}<em>2} + \overset{(A_m)}{\text{HOOC}} \overset{k_4}{\Rightarrow} \overset{(A</em>{n+m})}{\text{NHCO}} \overset{(W)}{\Rightarrow} \overset{k_4'}{\text{H}_2\text{O}} ]</td>
</tr>
<tr>
<td>[ \overset{(A_{n+m})}{\text{NHCO}} \overset{(W)}{\Rightarrow} \overset{(A_{n+m})}{\text{H}_2\text{O}} ]</td>
</tr>
</tbody>
</table>
reaction engineering viewpoint, however, several features are important. First of all, it has been shown that this reaction is catalyzed by chain end groups \((\text{BSi})\) which change in concentration with reaction conversion. This imparts an autocatalytic character to the reaction. Secondly, this polymerization has both step growth and chain growth character (11). There are essential differences in the general types of molecular weight distributions \((\text{MWD})\) obtained in idealized step growth and chain growth polymerizations. The question of MWD will be dealt with in more detail later in this paper. Thirdly, the reversibility of all the polymerization steps presents a mathematical challenge in modelling the system (12).

Caprolactam can also be readily polymerized by a variety of anionic initiators (5, 13-16). The attractiveness of this type process lies in the speed of the reaction. The mechanism is entirely chain growth. This time advantage is largely negated, however, by the necessity of allowing the narrow distribution product to re-equilibrate to the apparently desirable most probable distribution (15, 17). This factor, plus the necessity of maintaining scrupulously anhydrous conditions, makes this a little used reaction commercially (18). By application of the techniques demonstrated in this paper anionic polymerization of \(\varepsilon\)-caprolactam can be made a tractable mathematical modeling problem. However, the remainder of this paper is devoted to the hydrolytic process, a more commercially interesting system.

**MODELING TECHNIQUE**

The hydrolytic process of Table 1 can be represented in the following manner:

\[
\begin{align*}
M + W & \rightarrow S_1 \\
S_n + S_m & \rightarrow S_{n+m} + W \\
S_n + M & \rightarrow S_{n+1} \\
S_n + A_m & \rightarrow A_{n+m} + W
\end{align*}
\]

**Batch Reactor**

The molecular rate equations for the disappearance of the various species can be written as follows:

\[
\frac{dM}{dt} = -k_1MW + k_1'S_1
\]

\[
- k_2'M \sum_{n=1}^{\infty} S_n + k_5' \sum_{n=1}^{\infty} S_{n+1}
\]

\[
\frac{dS_1}{dt} = k_1'MW - k_1'S_1 - k_5S_1 \sum_{n=1}^{\infty} S_n
\]

\[
+ k_5'W \sum_{n=1}^{\infty} S_{n+1} + \sum_{n=1}^{\infty} A_n
\]

\[
\frac{dS_n}{dt} = (k_1'MW - k_1'S_{n-1}) \delta <n-1>
\]

\[
+ \frac{k_2'}{2} \sum_{m=1}^{n-1} S_{n-m}M_s - k_3'S_{n+1}
\]

\[
- k_2'W(S_n - S_1 \delta <n-1>) + k_3'M(S_n - S_{n-1})
\]

\[
+ k_5'S_1 \delta <n-1>- k_5S_n \sum_{m=1}^{\infty} A_m
\]

\[
\frac{dA_1}{dt} = -k_4A_1 \sum_{n=1}^{\infty} S_n + k_4'W \sum_{n=1}^{\infty} A_{n+1}
\]

\[
\frac{dA_n}{dt} = k_4 \sum_{m=1}^{\infty} S_{n-m}A_m - k_4A_n \sum_{m=1}^{\infty} S_m
\]

\[
- k_4'W(A_n - A_1 \delta <n-1>) + k_4'W \sum_{j=n+1}^{\infty} A_j
\]

where the function:

1. This term is not exactly correct since an \(S_1\) molecule does not result from every reaction between water and a polymer chain. The correct term is \(k_2'W \sum S_n/n\). Unfortunately, it cannot be easily transformed to give the correct term in the moment equations to be developed presently. However, it is apparent that the correct term is some fraction of the term which has been used. Our term represents an upper bound. The small magnitude of the rate constant \(k_2'\) (see Table 2) argues for the acceptance of this approximation.

2. Solution of this set of equations including this term requires assuming that \(S_1 \approx S_2\) which has been used previously (5) and is acceptable since both concentrations are quite small. Alternatively, it could be ignored altogether which has also been done in some theoretical studies of reversible polymerization (12).

3. This term gives the proper statistical weight to the hydrolysis reaction of water with the specific amide linkage in a molecule of size \(i\) which will just give a molecule of size \(n\).
At this point we introduce the discrete transformation of a function (21):
\[
G[f(n)] = \sum_{n=1}^{\infty} s^n f(n)
\]

hence:
\[
G(S_n) = \sum_{n=1}^{\infty} s^n S_n = P(s),
\]
\[
G(A_n) = \sum_{n=1}^{\infty} s^n A_n = A(s).
\]

Application of this transformation to Eqs 5-10, yields the following transformed equations:
\[
\frac{dM}{dt} = -k_1 M W + k_1' S_1 - k_3 M \mu_0 + k_3' \mu_0 - k_4 S_1
\]
\[
\frac{dW}{dt} = -k_1 M W + k_1' S_1 + \frac{k_2}{2} \mu_0^2 - k_2' W \mu_0
\]
\[
+ k_2' W S_1 + k_3' \mu_0' - k_4' W (\mu_0' - A_1)
\]
\[
\frac{dS_1}{dt} = k_3 M W - k_3' S_1 - k_3 S_1 \mu_0 + k_2' W (\mu_0 - S_1)
\]
\[
- k_3 M S_1 + k_3' S_1 - k_3 S_1 \mu_0' + k_4' W (\mu_0' - A_1)
\]
\[
\frac{dA_1}{dt} = -k_4 A_1 \mu_0 + k_4' W (\mu_0' - A_1)
\]
\[
\frac{dP(s)}{dt} = (k_1 M W - k_1' S_1) s + \frac{k_2}{2} P(s)^2 - k_2' P(s) \mu_0 - k_4' W (P(s) - s S_1)
\]
\[
+ 2k_4' W G \left[ \sum_{j=1}^{\infty} \frac{S_j}{j-1} \right] + k_3 M (s P(s) - P(s))
\]
\[
- k_3' \left( P(s) - \frac{1}{s} P(s) + S_1 \right) + k_3 S_1 s - k_4 P(s) \mu_0'
\]
\[
+ k_4' W G \left[ \sum_{j=1}^{\infty} \frac{A_j}{j-1} \right]
\]
\[
\frac{dA(s)}{dt} = k_4 A(s) P(s) - k_4 A(s) \mu_0
\]
\[
- k_4' W (A(s) - s A_1) + k_4' W G \left[ \sum_{j=n+1}^{\infty} \frac{A_j}{j-1} \right]
\]

where \(\mu_0\) and \(\mu_0'\) are the zeroth moments of the S and A distributions, respectively.

Our objective being to obtain as much information as possible about the molecular weight distribution, in addition to molecular weight and conversion information, there are several ways to approach the extraction of this information from Eqs 5 to 19. First of all, it should be pointed out that the product distribution obtained from this reaction scheme will be the sum of the distributions of unterminated and monofunctionally terminated species. If the set of Eqs 14 to 19 could be solved to give analytical expressions for \(P(s)\) and \(A(s)\), the inverse transformation could be applied to these functions, and analytical expression obtained for MWD as a function of time. An analytical solution in the present case is obviously quite out of the question. The alternative is to obtain the moments of the polymer chain length distribution (PCLD) defined by:
\[
\mu_k = \sum_{n=1}^{\infty} n^k S_n, \mu'_k = \sum_{n=1}^{\infty} n^k A_n
\]

and work with some measure of the character of the product MWD defined in terms of its moments, \(\mu_k^p = \mu_k + \mu'_k\). The simplest function to characterize the MWD is the polydispersity or dispersion index \(Z_p\) defined by:
\[
Z_p = \frac{\mu_2}{\mu_1^p} = \frac{\mu_2^p/\mu_1^p}{\mu_2^p/\mu_0^p}
\]

Differential equations for the moments can be obtained by direct summation according to Eq 20 or by utilization of the moment generating property of the discrete transform (19, 21-23).
\[
\mu_k = s \to \frac{1}{C (\text{ln} s)^k}, \mu'_k = s \to \frac{1}{C (\text{ln} s)^k}. (22)
\]

Using the latter approach, differential equations for the moments of the PCLD were obtained:
\[
\frac{d\mu_0}{dt} = (k_1 M W - k_1' S_1) - \frac{k_2}{2} \mu_0^2 + k_2' W (\mu_0 - S_1)
\]
\[
- k_4' \mu_0' + k_4' W (\mu_0' - A_1)
\]
\[
\frac{d\mu_1}{dt} = (k_1 M W - k_1' S_1) + k_3 M \mu_0 - k_3' \mu_0 + k_3 S_1
\]
\[
- k_3' \mu_0' + \frac{k_4'}{2} W (\mu_0' - A_1)
\]
\[
\frac{d\mu'_1}{dt} = k_4' \mu_0' - \frac{k_4'}{2} W (\mu_0' - A_1)
\]
\[
\frac{d\mu_2}{dt} = (k_1 M W - k_1' S_1) + k_2 \mu_0^2 - k_4' W (\mu_2 - S_1)
\]
\[
+ \frac{k_4'}{3} W (2 \mu_2 - \mu_1 - S_1) + k_3 M (2 \mu_2 + \mu_0)
\]
\[
- k_3' (2 \mu_2 - \mu_0) + k_5' S_1 - k_4' \mu_0' \mu_2
\]
\[
+ \frac{k_4'}{6} W (2 \mu_2' - \mu_1' - A_1)
\]
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\[ \frac{d\mu_j^e}{dt} = k_4(2\mu_j^e\mu_1^e + \mu_0^e\mu_2^e) - k_4'W(\mu_j^e - A_i) + \frac{k_4'}{6}W(2\mu_0^e - \mu_j^e - A_i) \] (28)

The treatment of the terms involving \( G \left[ \sum_{j=n+1}^\infty \frac{S_j}{j-1} \right] \), and the corresponding term for \( A_i \), required a summation approach detailed in Appendix A. Equations 14-17 and 23-28 comprise a closed set of simultaneous, nonlinear, ordinary differential equations which were solved numerically using a fourth order Runge-Kutta routine.

As pointed out earlier, this reaction is catalyzed by chain ends, so we have...

\[ k_i = k_0 + k_{i,c}e^p \] (29)

...for each of the four forward and reverse reactions. The rate constants and equilibrium constants used in this summation approach detailed in Appendix A. Table 2. Rate and Equilibrium Constants for Caprolactam Polymerization at 220°C.

<table>
<thead>
<tr>
<th>i</th>
<th>( k_{10} ) (kg hr(^{-1}) mole(^{-1}))</th>
<th>( k_{1c} ) (kg(^2) hr(^{-1}) mole(^{-2}))</th>
<th>( k_i )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>( 8.0 \times 10^{-4} )</td>
<td>0.17</td>
<td>2.2 \times 10^{-3}</td>
</tr>
<tr>
<td>2</td>
<td>0.9</td>
<td>20.0</td>
<td>8.5 \times 10^{2}</td>
</tr>
<tr>
<td>3</td>
<td>1.0</td>
<td>21.0</td>
<td>1.9</td>
</tr>
<tr>
<td>4</td>
<td>0.9</td>
<td>20.0</td>
<td>8.5 \times 10^{2}</td>
</tr>
</tbody>
</table>

* Taken from (7-9).

Continuous Stirred Tank Reactor

For micromixed CSTR's, the mass balance equations may be written directly from the batch reactor Eqs 5-10 by incorporation of the inflow-outflow terms, i.e., \((M_{\text{in}} - M_{\text{out}})/\theta\), etc., where \( \theta \) is the average residence time. For steady state operation, the time derivatives vanish. The equations are transformed and the moment equations developed in a manner paralleling that for the batch reactor. Non-linear algebraic equations result which are solved by a Newton-Raphson method. The complete set of CSTR equations is given in Appendix B.

RESULTS AND DISCUSSION

Batch Reactor

Figures 1 and 2 compare the model presented in this paper to the published data of Hermans, et al (7). We find quite a good fit to the experimental data, especially in the initial portions of the curves. Along with the conversion curve in Fig. 3, these curves demonstrate the autocatalytic nature of this reaction. The overall reaction is relatively slow until the ring-opening has proceeded to a sufficient extent. For this reason, some of the ideas of Kilkson (25) with regard to the concept of slow influx in polycondensation reactions apply to this reaction. The highest rate of conversion roughly corresponds to the maximum in the \( \mu_0 \) curve.

As pointed out by Hermans, et al (7), the changing nature of the reaction medium from predominantly caprolactam to predominantly polymer, makes determination of rate constants which apply over the entire conversion range very difficult. The rate constants we have used, given in Table 2, are a combination of those of Hermans (7) and Wiloth (8,9). This model may provide a means to determining con-

![Fig. 1. Monomer concentration vs time in a batch reactor at three initial water concentrations: (○) \( W_{W}/M_0 = 0.05 \); (●) \( W_{W}/M_0 = 0.067 \); (□) \( W_{W}/M_0 = 0.1 \). M is in mole kg\(^{-1}\); A = 0. Symbols are experimental data of Hermans, et al (7). Solid line is predicted curve.](image-url)
stants that provide the statistical best fit to a given set of data over the entire conversion range. We did not attempt to optimize the fit to the data in this manner, however.

Two reactions not considered in the model may contribute to the discrepancy between the predicted curves and the data. The first is a cyclization reaction which, although similar in mechanism to the reverse reaction 3, produces not monomer but cyclic oligomers. Indeed, commercial products do contain these species in minute amounts up to a cyclic nonomer (18). If kinetic data were available (namely, cyclization constants) this reaction, or an approximation to it, could be treated by our model, similar to the treatment of Mochizuki and Ito (26). The other reaction not considered is the transamidation reaction. It is difficult to assess a priori the effect of this reaction. Some kinetic data are available (5) but inclusion of this reaction in a kinetic model would be extremely difficult.

Figure 3 gives conversion versus time, as well as the development of degree of polymerization and MWD, for a typical initial water concentration with and without monofunctional acid. Addition of monofunctional acid somewhat decreases the time for attainment of the equilibrium conversion. The molecular weight controlling effect is demonstrated by the $\bar{M}$ versus time curve. Considering now the molecular weight distribution, we note that a value of 2.0 is characteristic of a most probable distribution. Except for a plateau at about 1.75 in the early stages of the reaction where polymerization is dominated by the chain growth mechanism polyaddition, the value of 2.0 is approached as the equilibrium conversion is neared. It is seen also that addition of small amounts of monofunctional acid is predicted to broaden the MWD somewhat, especially in the early stages of polymerization. As with any theoretical result, the validity of the prediction is difficult to argue in the absence of some of the experimental results it seeks to predict. This suggests that an experimental investigation of MWD versus conversion would be interesting.

The CSTR

Figures 4 and 5 describe the polymerization in a CSTR. We see that very broad distribution product may be obtained in a CSTR, consistent with the partial step growth character of the polymerization (19, 23). No data on continuous caprolactam polymerization are available for direct comparison. In Fig. 5 it is seen that control of product molecular weight and MWD can be obtained by addition of 0.25 to 1.0 percent monofunctional acid.

One final point with respect to the CSTR is that we have assumed perfect mixing. If some degree of segregation had been introduced, the prediction would probably be a narrower PCLD in keeping with the general results for condensation polymerizations (19, 23).

Series Configurations

A primary advantage of this deterministic model is demonstrated in treatment of series reactor configurations. Tables 3-5 deal with various plug flow reactor-CSTR schemes for producing nylon-6 continuously. Equal reactor volumes are considered with
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I.

**Fig. 4.** Predicted curves for \( x, \mu_0 \) (m/kg \( \times 10^3 \)), \( \bar{D}P_n \), and \( Z_p \) vs residence time in a CSTR at various initial water concentrations: (a) \( W_o/M_o = 0.01 \); (b) \( W_o/M_o = 0.05 \); (c) \( W_o/M_o = 0.1 \).

The space time, \( \tau \), required to give the specified product after each stage shown. With no water removal, using as acceptable product criterion a \( \bar{D}P_n \) of 150,

**Table 3. Two Reactor Schemes, PFR-CSTR in Series**

<table>
<thead>
<tr>
<th>First reactor: PFR effluent specifications</th>
<th>Water removal after first reactor</th>
<th>Second reactor: CSTR effluent specifications</th>
<th>Total space time (hrs.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \bar{D}P_n )</td>
<td>( x )</td>
<td>( Z_p )</td>
<td>( \tau_1 ) (hrs.)</td>
</tr>
<tr>
<td>1</td>
<td>50</td>
<td>0.52</td>
<td>1.56</td>
</tr>
<tr>
<td>2</td>
<td>100</td>
<td>0.84</td>
<td>1.18</td>
</tr>
<tr>
<td>3</td>
<td>50</td>
<td>0.52</td>
<td>1.56</td>
</tr>
<tr>
<td>4</td>
<td>100</td>
<td>0.84</td>
<td>1.18</td>
</tr>
</tbody>
</table>

* \( W_o/M_o = 0.05 \).

**Table 4. Two Reactor Schemes, CSTR-PFR in Series**

<table>
<thead>
<tr>
<th>First reactor: CSTR effluent specifications</th>
<th>Water removal after first reactor</th>
<th>Second reactor: PFR effluent specifications</th>
<th>Total space time (hrs.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \bar{D}P_n )</td>
<td>( x )</td>
<td>( Z_p )</td>
<td>( \tau_1 ) (hrs.)</td>
</tr>
<tr>
<td>1</td>
<td>50</td>
<td>0.41</td>
<td>2.67</td>
</tr>
<tr>
<td>2</td>
<td>100</td>
<td>0.70</td>
<td>4.64</td>
</tr>
<tr>
<td>3</td>
<td>50</td>
<td>0.41</td>
<td>2.67</td>
</tr>
<tr>
<td>4</td>
<td>100</td>
<td>0.70</td>
<td>4.67</td>
</tr>
</tbody>
</table>

* \( W_o/M_o = 0.05 \).

It is seen that either series configuration can be used to obtain a similar product at comparable residence times. The key point is that it is not recommended to try to obtain high conversion in the CSTR section. The largest part of conversion and growth should
occur in the PFR with the CSTR used as a starting or finishing reactor. These same general rules hold for the cases of complete water removal after the first stage. Water removal does give a considerable process time advantage in agreement with results obtained by other workers (2, 3). This is further demonstrated in Table 5 where two PFR's in series are run with water removal between stages. This configuration has interest since it is the limiting case of an infinite series arrangement of CSTR's. These results show that it is desirable to remove water from the reaction as early in the process as possible. However, we would not expect it to be desirable to remove the water at a residence time lower than the point at which the maximum in the $\mu_0$ curve occurs. The proper choice of series configuration can provide a considerable improvement over a single CSTR.

In summary, the deterministic model developed in this paper has been applied to various single and series reactor configurations. From this model predictions about MWD as well as molecular weight distributions other than most probable result in many cases. Some tuning of the model is indicated to improve the agreement between the model and the available data. A more systematic approach to determining the optimal reactor configuration through the use of this model is likely to prove quite fruitful.

**NOMENCLATURE**

\[ A_i = \text{concentration of monofunctional species of chain length } i \text{ (mole kg}^{-1}) \]

\[ \overline{DP}_n = \text{number average degree of polymerization} \]

\[ \overline{DP}_w = \text{weight average degree of polymerization} \]

\[ k_i = \text{forward rate constant of } i\text{th reaction} \]

\[ k_i' = \text{reverse rate constant of } i\text{th reaction} \]

\[ \overline{K}_i = \text{equilibrium constant of } i\text{th reaction} \]

\[ M = \text{concentration of caprolactam (mole kg}^{-1}) \]

\[ S_i = \text{concentration of difunctional species of chain length } i \text{ (mole kg}^{-1}) \]

\[ W = \text{concentration of water (mole kg}^{-1}) \]

\[ Z_p = \text{polydispersity} = \overline{DP}_w/\overline{DP}_n \]

\[ \mu_0 = \text{$k^{10}$ moment of the distribution of chain lengths of monofunctional species} \]

\[ \mu_0' = \text{$k^{10}$ moment of the distribution of chain lengths of monofunctional species} \]

**REFERENCES**


19. R. L. Lawrence, unpublished manuscript.


**APPENDIX A**

It can be shown that

\[
G \left( \prod_{j=1}^{\infty} \frac{S_j}{f-1} \right) = \frac{1}{1-s} \left\{ \lim_{s' \to 1} \left[ s' \int_0^{\infty} \frac{P(s')}{(s')^2} \, ds' \right] \right\}
\]

This is not easily converted to a moment equation. However, since moment equations are the objective of applying the transformation, they can be obtained in an equivalent but different form by expanding the double summation and recombining. We have

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\[ \mu_k = \sum_{n=1}^{\infty} n^k S_n \]  \hspace{1cm} (A-2)

Therefore, the following expressions can be evolved and substituted into equations for the appropriate order moment

\[ \sum_{n=1}^{\infty} \sum_{j=n+1}^{\infty} \frac{S_j}{j-1} = \mu_0 - S_1 \]  \hspace{1cm} (A-3)

\[ \sum_{n=1}^{\infty} n \sum_{j=n+1}^{\infty} \frac{S_j}{j-1} = \frac{1}{2} (\mu_1 - S_1) \]  \hspace{1cm} (A-4)

\[ \sum_{n=1}^{\infty} n^2 \sum_{j=n+1}^{\infty} \frac{S_j}{j-1} = \frac{1}{6} (2\mu_2 - \mu_3 - S_1) \]  \hspace{1cm} (A-5)

An identical treatment is used for the corresponding \( A_j \) term.

**APPENDIX B**

Equations for CSTR:

\[ \frac{M_t - M_0}{\theta} = -k_3 W + k_3'S_1 - k_0 M_{\mu_0} \]

\[ + k_3' \mu_0 - k_3'S_1 \]  \hspace{1cm} (B-1)

\[ \frac{W_t - W_0}{\theta} = -k_1 W + k_1'S_1 + \frac{k_2}{2} \mu_0^2 - k_2' W_{\mu_0} \]

\[ + k_2' W S_1 + k_3' \mu_0' - k_4' W (\mu_0' - A_1) \]  \hspace{1cm} (B-2)

\[ \frac{S_{1t} - S_{10}}{\theta} = k_1 M W - k_1'S_1 - k_2 S_{\mu_0} \]

\[ + k_2' W (\mu_0 - S_1) - k_3'M S_1 + k_3'S_2 - k_3 S_{\mu_0'} \]

\[ + k_4' W (\mu_0' - A_1) \]  \hspace{1cm} (B-3)

\[ \frac{A_{11} - A_{10}}{\theta} = -k_4 A_{1\mu_0} + k_4' W (\mu_0' - A_1) \]  \hspace{1cm} (B-4)

\[ \frac{\mu_{11} - \mu_{10}}{\theta} = k_1 M W - k_1'S_1 - \frac{k_2}{2} \mu_0^2 \]

\[ + k_2' W (\mu_0 - S_1) - k_3'M \mu_0' + k_4' W (\mu_0' - A_1) \]  \hspace{1cm} (B-5)

\[ \frac{\mu_0' - \mu_0'}{\theta} = 0 \]  \hspace{1cm} (B-6)

\[ \frac{\mu_{11} - \mu_{10}}{\theta} = k_1 M W - k_1'S_1 + k_3 M \mu_0 \]

\[ - k_3' \mu_0 + k_3'S_1 - k_4' \mu_0' + \frac{k_4}{2} W (\mu_0' - A_1) \]  \hspace{1cm} (B-7)

\[ \frac{\mu_{11} - \mu_{10}'}{\theta} = k_4' \mu_0' - \frac{k_4}{2} W (\mu_0' - A_1) \]  \hspace{1cm} (B-8)

\[ \frac{\mu_{21} - \mu_{20}}{\theta} = k_1 M W - k_1'S_1 + k_2 \mu_0^2 \]

\[ - k_2' W (\mu_0 - S_1) + \frac{k_3}{3} W (2\mu_2 - \mu_1 - S_1) \]

\[ + k_3'M (2\mu_1 + \mu_0) - k_3' (2\mu_1 - \mu_0) + k_3'S_1 \]

\[ - k_4' \mu_0' + \frac{k_4}{6} W (2\mu_2' - \mu_1' - A_1) \]  \hspace{1cm} (B-9)

\[ \frac{\mu_{22} - \mu_{20}}{\theta} = k_4 (2\mu_1 \mu_1' + \mu_0' \mu_2) - k_4' W (\mu_2' - A_1) \]

\[ + \frac{k_4}{6} W (2\mu_2' - \mu_1' - A_1) \]  \hspace{1cm} (B-10)