Thermal Degradation of Starch in Production of Environmentally Benign Flocculants. 1. Stochastic Modeling of Degradation Process

János Gyenis,*,† Judit Dencs,‡ Gábor Nös,‡ and Gyula Marton‡

Research Institute of Chemical and Process Engineering and Department of Chemical Engineering, University of Pannonia, Egyetem u. 8, H-8200 Veszprem, Hungary

The paper deals with the thermal degradation of starch during phosphorylation carried out at elevated temperatures in the solid phase to produce biodegradable flocculants. The aim of the work reported here was to elucidate the mechanism and kinetics of the degradation process. In the first part of this study, a discrete Markov-chain model was proposed and discussed. The whole molecular weight range of the raw material and degradation products was divided into 10 discrete intervals. Mass transitions between them were considered as the consequence of splits of molecules to fragments, occurring with given probabilities at different positions within the molecules during a time step. Supposing various distributions of split probabilities along the length of starch molecules, and considering different influences of molecular weights on these probabilities, simulations were carried out resulting in characteristic patterns in the evolution of molecular weigh distributions during the process. These characteristics made it possible to identify the mechanism of degradation.

Introduction

Starch is a natural polymer available in plants, which can be used as raw material to produce various biodegradable products. Recently, chemical modification of starch was proposed by Dencs et al. to prepare environmentally friendly flocculants applicable in water purification processes.[1,2] Chemical modification was carried out at elevated temperature in the solid state with sodium diammonium phosphate and a nitrogen-containing catalyst resulting in simultaneous phosphorylation and breakage of starch molecules. A certain degree of degradation is necessary to convert the product water-soluble, but excessive degradation may influence the product quality disadvantageously causing reduction in flocculation efficiency. To prepare high-performance flocculants, the highest possible molecular weight should be protected that is still soluble in water. For this purpose, the conditions of treatment, especially temperature, pH, and processing time, are to be optimized. Together with experimental investigation, the modeling of process helps to achieve this objective.

During the last decades, several papers have been published on heat degradation of various polymers, but only a few of them dealt with starch. A considerable part of these studies presumed a great number of chemical reactions leading to complicated models not too easy to solve. Mehl et al.[3] applied a kinetic model to study the thermal degradation of halogenated polymers where the proposed mechanism took 38 species into account in ∼190 reactions. Marongiu et al.[4] investigated the same problem, supposing 40 species in ∼250 reactions. Staggs[5] developed a mathematical model for random scission of linear polymer chains composed of a high number of differential equations to describe the evolution of molecular weight distributions as a function of the fraction of bonds broken. In another work,[6] Monte Carlo simulation was used to analyze the changes of the population of molecules undergoing end-chain scission and simultaneous recombination. For this, a molecule was selected from a distribution of molecules at random and allowed to split to a monomer and a new molecule with one fewer repeat units. Kostoglou[7] also emphasized the importance of the end-chain scission mechanism. Madras[8] investigated the rate of degradation of PMMA dissolved in toluene at different temperatures. In his work, a discrete model of polymer degradation was derived and compared to the approach of continuous kinetics. In another study,[9] a random chain scission mechanism was supposed, where the rate of polymer decomposition depended on the chain length.

Platkowski and Reichert[10] used the Monte Carlo method for modeling of polymerization and thermal degradation. Ziff and McGrady[11] studied the effect of the size distribution of polymers and found that the rate of bond scission depended on the chain length and on the position of the bond within the chain. A model was proposed where the bonds break preferentially in the center with a parabolic probability distribution along the chain. A Monte Carlo study on the degradation of highly branched polymer molecules was published by Galina and Lechowicz.[12] The aim was to verify whether a bond scission led to a split of a molecule in two smaller ones or just to reduction of the number of monomer units in the molecule. Emsley and Heywood[13] used a pseudorandom number generator to choose splitting bonds randomly. In one of their case studies, the degradation of cellulose was investigated in water at ambient temperatures. It was pointed out that totally random distribution did not explain the experimental observations, but supposing a mechanism with systematic scission of the polymer chains resulted in much better agreement. Nassar et al.[14] used the Markov-chain approach for the analysis of a stepwise enzymatic cellulose degradation. Their model predicted the length distribution of cellulose molecules obtained by hydrolysis after different times.

It seems from the literature that the majority of papers proposed deterministic models to study polymer degradation, and only a few of them used a stochastic approach, mostly Monte Carlo simulation. However, in other fields of chemical engineering, stochastic models were more common, applying, for example, Markov-chain models for bulk solids mixing.[15−18] The process of particle attrition was modeled by Duggirala and Fan[19] proposing a cell model with probability balance equation. Berthiaux[20] developed a Markov-chain model to investigate the particle size distribution in grinding. As regards modeling principles, particle breakage is similar to molecule degradation.

---

* To whom correspondence should be addressed. E-mail: gyenis@mukki.richem.hu. Tel: : +36-88-624-032. Fax: +36-88-624-038.

† Research Institute of Chemical and Process Engineering.

‡ Department of Chemical Engineering.

10.1021/ie061365g CCC: $37.00

Therefore, these latter works gave inspiration to develop a Markov-chain model to investigate the process of starch degradation.

The starting point of our study was that, similar to the breakage of particles, the thermal degradation of starch molecules cannot be considered as a deterministic process. On the other hand, starch is a natural polymer with varying and not exactly known chemical composition. Therefore, stochastic modeling, first the Markov-chain approach, has great potential in this field. The main advantages of this latter are as follows: (1) less preliminary knowledge is needed on the exact composition of starch and on its degradation products, and (2) the model and its solution are essentially simpler compared to the usual deterministic approach.

Modeling Aims and Principles

During the experiments described in the second part of this study (preceding paper in this issue), it was found that the molecular weights of the product could be controlled by the duration and temperature of the treatment. Because the molecular weight distribution is of primary importance from the respect of flocculation efficiency, and is influenced by the mechanism of degradation, the aim of the first part of our study was to elucidate the relationship between the mechanism and the resulting molecular weight distributions. Knowing this relationship, the objective of the second part of the work was to identify the mechanism and kinetics of degradation from data obtained experimentally.

Preliminary Considerations. Due to the complex behavior and composition of starch in the studied process, some basic considerations and simplification had to be made as follows:

(1) Split of a molecule among the multitude of molecules is a stochastic event; i.e., it can happen accidentally. The probability of its occurrence in a given time interval depends on the chemical structure, energy state, and interactions of molecules with their environment. Some influencing factors are presence and concentration of reagents and catalysts, temperature, pressure, pH, etc. The proposed stochastic model did not require the preliminary or exact knowledge of these effects.

(2) Considering that starch molecules are long carbohydrate chains, the location of bond scission can be accidental, too. This means that cutting off sections of various lengths from the chain can happen with different probabilities. In other words, split probabilities are not necessarily identical at every location in the chain; i.e., they may have a distribution along the length of a molecule.

(3) Due to the multitude of molecules in the reaction mixture, the distribution of molecular weights can be considered as continuous. However, dividing the studied molecular weight range into discrete intervals, the distribution can be given in the form of a histogram. In the proposed stochastic model, these MW intervals are not necessarily uniform; linear and nonlinear divisions are equally applicable.

(4) Due to splitting, the fragments of a molecule are transferred from its original MW interval to lower ones. Therefore, due to the transitions, the number of molecules in various MW intervals, i.e., molecular weight distribution of the reaction mixture, is changing during the process.

(5) The transitions from a given MW interval to other ones depend on the actual conditions only; i.e., the earlier molecular weight distributions have no influence on the actual transitions. Therefore the process can be considered as a homogeneous Markov chain.

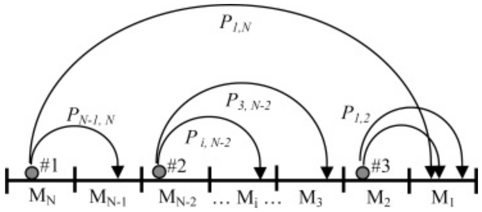

Figure 1. Principle of the proposed model.

(6) The differences in the chemical structures and molecular weights of molecules within a given MW interval are neglected. Therefore, the deviations of split probabilities within an interval are also ignored.

(7) The law of mass conversation should be respected. For this, the split probabilities (determining the number transition probabilities to other intervals) have to be converted to mass fraction transition probabilities. The mass balances of the whole system and for each MW interval separately should be considered.

(8) The continuous time scale of treatment was discretized using uniform time steps. To investigate the behavior of the proposed model in this first part of the paper, it was supposed that a molecule splits only once and to two parts during a time step. In the second part of the study, to determine the transitions between the MW intervals from experimental data, this supposition was not required.

(9) For the sake of simplicity it was supposed that no coupling of molecules (polymerization or cross-linking) takes place in this process. If however coupling would also occur, this can be taken into account by using net values for transition probabilities.

The explanation of modeling principles is shown in Figure 1. Let us consider a molecular weight range extending between the maximal MW in the original starch and the lowest value in the degradation product. Let us divide this scale into smaller intervals arbitrarily, considering the desired scrutiny and the applied analytical method. These intervals are distinguished by their characteristic (e.g., mean) molecular weight M_i, where index i decreases with decreasing molecular weights from M_N to M_1. Because the process is considered as homogeneous Markov chain and modeling can be started at any stage of degradation, M_N means the highest MW interval at the beginning of calculation.

The split probability of molecules in interval M_i during time step Δt is denoted by ${}_nP_i$. Because the reaction mixture contains a great number of molecules, due to the law of large numbers, this probability gives the expected proportion of molecules that will split in interval M_i during time step Δt. Index n on the left side of ${}_nP_i$ indicates that it refers to the number of molecules.

Let us suppose a molecule in interval M_N marked by #1 in Figure 1 that splits in two fragments transferred to M_{N-1} and M_1, respectively. Particles #2 and #3 are similar examples for other splitting molecules. The mass balance for molecule #1 is $m_N = m_{N-1} + m_1$. In general, for any splitting molecule

$$m_k = m_l + m_m \tag{1}$$

where m_k, m_l and m_m are the masses of the parent molecule and the resultant fragments belonging to intervals M_k, M_l and M_m, respectively. Because the parent molecule decomposes to two parts, birth probabilities of fragments ${}_nP_{l,k}$ and ${}_nP_{m,k}$ should be identical and equal to split probability ${}_nP_k$ as

$${}_nP_k = {}_nP_{l,k} = {}_nP_{m,k} \tag{2}$$

However, the masses of fragments transferred to intervals M_l and M_m are generally not identical because m_1 and m_n can differ

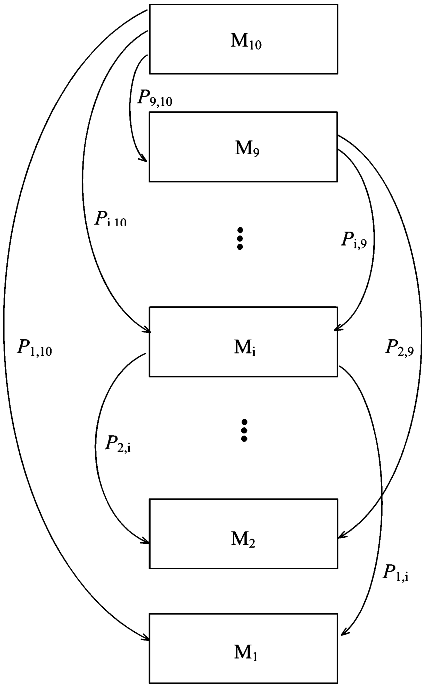

Figure 2. Graph representation of the model structure.

from each other. It means that mass transition probabilities differ from the number transition probabilities as will be shown later.

If in an ith MW interval during time step Δt, splitting of several molecules takes place simultaneously and ${}_nP_{j,i}$ denotes the transition probability of a molecule fragment from interval i to interval j, the degradation probability of molecules in interval i is

$$ {}_nP_i = \sum_{j,j\neq i} {}_nP_{j,i} \tag{3} $$

The so-called self-loop probability ${}_nP_{i,i}$ tells us the chance that a molecule in interval i will not split; i.e., it remains in interval M_i. As ${}_nP_{i,i}$ and ${}_nP_i$ are complementary quantities

$$ {}_nP_{i,i} = 1 - \sum_{j,j\neq i} {}_nP_{j,i} \tag{4} $$

Calculation with transferred mass fractions instead of the number of fragments is more reasonable in practice. Using mean molecular weights M_j or M_k instead of m_j and m_k as approximation, the conversion between number and mass transition probabilities is

$$ P_{j,i} = \frac{M_j \cdot {}_nP_{j,i}}{\sum_k M_k \cdot {}_nP_{k,i}} \tag{5} $$

where $P_{j,i}$ is the mass fraction transition probability from an ith to the jth interval, while ${}_nP_{j,i}$, and ${}_nP_{k,i}$ are the number transition probabilities from the ith interval to the jth and to any kth intervals, respectively, including $k = j$. Approximation $M_i \cong m_i$ can be applied only if the MW intervals are uniform and narrow enough. In the second part of this study, where no conversion was done, this constraint was not required.

The change of the mass fraction of an ith MW interval during time step Δt can be calculated from mass balance

$$ \frac{\Delta x_i}{\Delta t} = \sum_{k,k\neq i} P_{i,k} \cdot x_k - x_i \cdot \sum_{j,j\neq i} P_{j,i} \tag{6} $$

Table 1. Types of Split Probability Profiles Used for Simulations

	split probability distribution along the length of molecules		
dependence on the size of molecules	case A uniform probability anywhere	case B increases toward the middle	case C increases toward the ends
case a no dependence	case Aa	case Ba	case Ca
case b linear decrease with decreasing size	case Ab	case Bb	case Cb
case c exponential decrease with decreasing size	case Ac	case Bc	case Cc

which is the difference between the mass fractions entering and leaving the ith MW interval, and x_i and x_k are the mass fractions of the ith and any kth ($k \neq i$) intervals averaged for the actual Δt time step. Mass fraction x_i is the mass of material in interval M_i per the total mass of the reaction mixture.

Model Development. Considering the complexity and stochastic behavior of the studied system, there is no reason to define too high a number of MW intervals. In this part of our study, the whole MW range was divided into 10 discrete intervals ($M_{10} > M_9 > M_8 > ... M_i ... > M_2 > M_1$). The structure of the model is shown in Figure 2, where the boxes and arrows represent the molecular weight intervals and the transitions between them, respectively. During degradation, transitions take place from higher to lower MW intervals only. For the sake of clarity, only a few transitions are indicated on the diagram as examples.

The first objective of modeling was to estimate the evolution of molecular weight distribution in the reaction mixture versus time testing different transition probability profiles along the length of molecules. The influence of the molecular weights of the splitting molecules was also investigated. The estimated molecular weight distribution, i.e., the expected mass fractions in different MW intervals ($p_i(t_n)$) after the nth time step was described by state probability vector $p(t_n)$ as

$$ p(t_n) = [p_{10}(t_n)\ \ p_9(t_n)\ \ ...\ p_n(t_n)\ \ ...\ p_2(t_n)\ \ p_1(t_n)] \tag{7} $$

where $\sum p_i(t_n) = 1$ at any time.

As was mentioned, calculation can be started at any stage of the process with any kind of initial distribution. To study the behavior of the proposed model, the initial state at $t = t_0$ was chosen as

$$ p(t_0) = [p_{10}(t_0)\ \ p_9(t_0)\ \ ...\ p_n(t_0)\ \ ...\ p_2(t_0)\ \ p_1(t_0)] = [1\ 0\ 0\ 0\ 0\ 0\ 0\ 0\ 0\ 0] \tag{8} $$

Similar to a commonly used method,[15−17] transition probabilities $P_{j,i}$ were arranged in matrix P, where diagonal elements $P_{i,i}$ are the so-called self-loop probabilities. $P_{1,1} = 1$ means that from the last interval M_1 no further degradation takes place.

$$ P = \begin{vmatrix} P_{10,10} & 0 & \cdots & 0 & \cdots & 0 & 0 \\ P_{9,10} & P_{9,9} & \cdots & 0 & \cdots & 0 & 0 \\ \vdots & \vdots & \cdots & 0 & \cdots & 0 & 0 \\ P_{i,10} & P_{i,9} & \cdots & P_{i,j} & \cdots & 0 & 0 \\ \vdots & \vdots & \cdots & \cdots & \cdots & 0 & 0 \\ P_{2,10} & P_{2,10} & \cdots & P_{2,j} & \cdots & P_{2,2} & 0 \\ P_{1,10} & P_{2,9} & \cdots & P_{1,j} & \cdots & P_{1,2} & 1 \end{vmatrix} \tag{9} $$

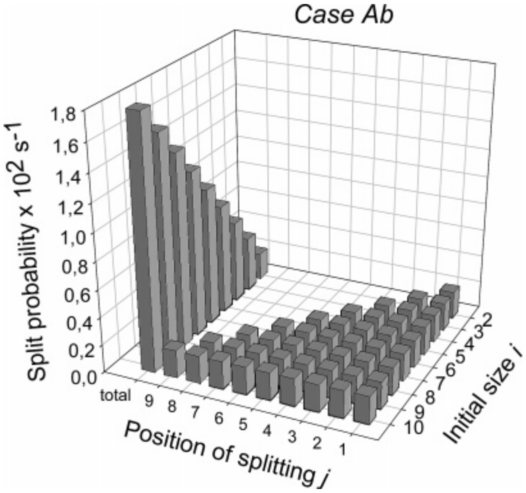

Figure 3. Split probability distribution used for case Ab.

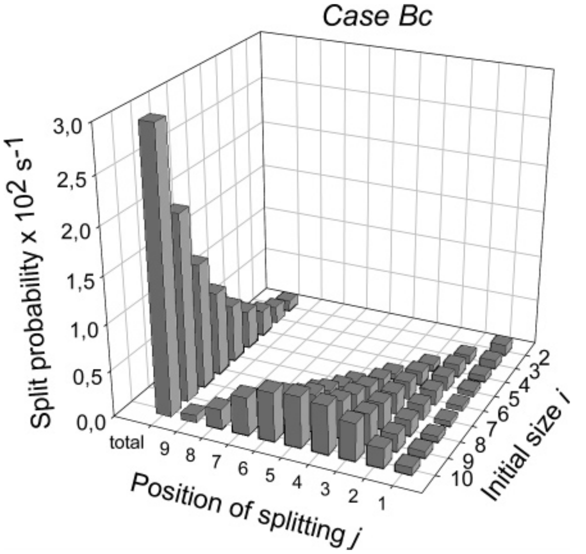

Figure 4. Split probability distribution used for case Bc.

There are two possibilities to calculate the time evolution of the expectable molecular weight distributions. At first, according to the practice applied in earlier studies,[15−17] the state probability after an nth time step can be calculated by matrix operation as

$$p(t_n) = p(t_0) \times P^n \tag{10}$$

In this work, another method was used, where transitions probabilities $P_{j,i}$ refer to the expectable mass fraction transitions per unit time. In this case, the transferred mass fraction from an ith to a jth interval during the nth time step is estimated as

$$\frac{\Delta x_{j,i}}{\Delta t} = p_i(t_n)\cdot P_{j,i} \tag{11}$$

The change of mass fraction in interval M_i can be determined from the mass balance. Writing eq 6 in differential form, and using p_i state probability instead of mass fraction x_i, the change of $p_i(t)$ is

$$\frac{dp_i}{dt} = \sum_{k,k\neq i}(P_{i,k}\cdot p_k(t)) - p_i(t)\cdot\sum_{j,j\neq i}P_{j,i} \tag{12}$$

Considering intervals M_{10}−M_1, the expected molecular weight distribution was determined by solving a differential equation system composed of 10 equations, with initial conditions shown in eq 8.

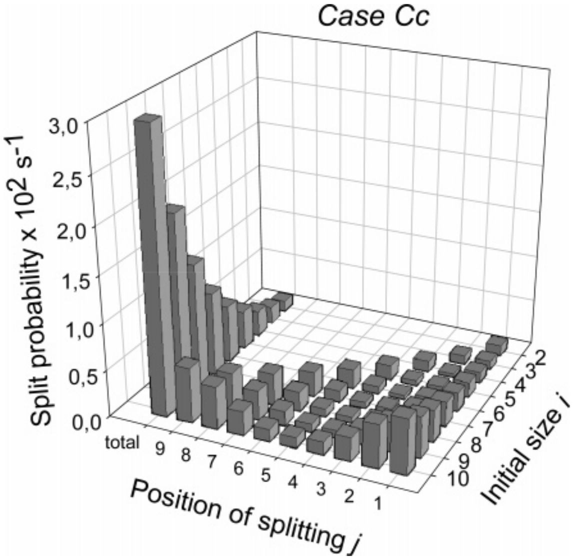

Figure 5. Split probability distribution used for case Cc.

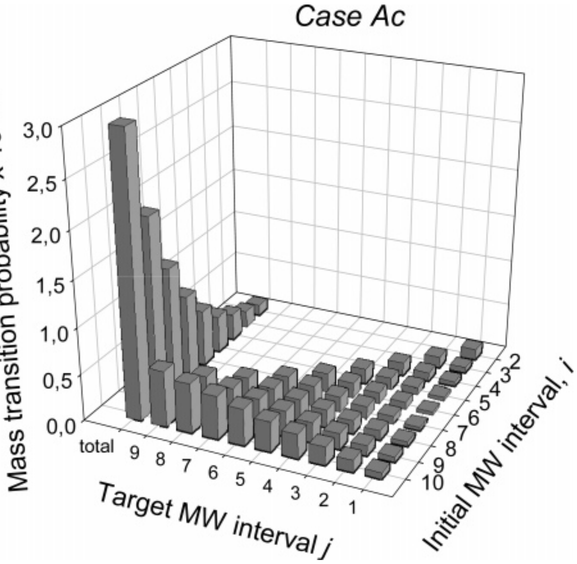

Figure 6. Mass fraction transition probabilities in case Ac.

Model Parameters. The first objective of simulation was to elucidate the influence of different split probability profiles on the expected evolution of molecular weight distribution during the process. For this, three different types of split probability distributions were considered along the length of molecules: case A−uniform probabilities along the whole length; case B−increasing probability toward the middle of the molecule chains; case C−increasing probability toward the ends (end scission is preferred).

To study the effect of the size of molecules, three different possibilities were considered: *case a*−equal degradation probability for any size; *case b*−linear decrease of $_nP_i$ with decreasing size; *case c*−exponential decrease with decreasing size.

The combinations of these suppositions are shown in Table 1. Simulations were carried out with all the nine possibilities, but among them only the most informative results will be discussed here. Figures 3−5 show the model parameters used for cases Ab, Bc, and Cc, respectively. The first horizontal axis in the forefront of these diagrams refers to the position of

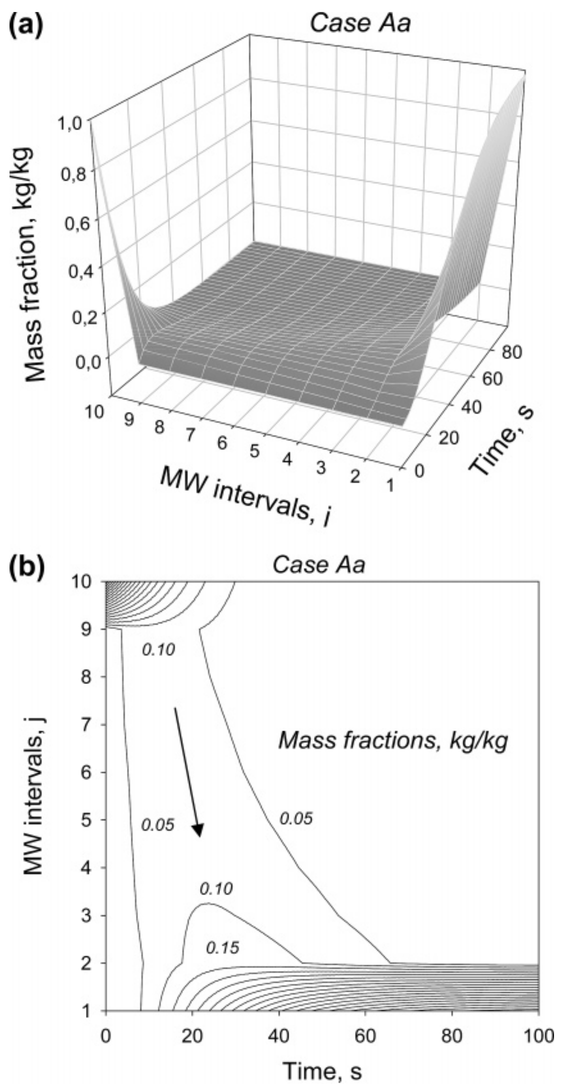

Figure 7. Evolution of MWD in case Aa.

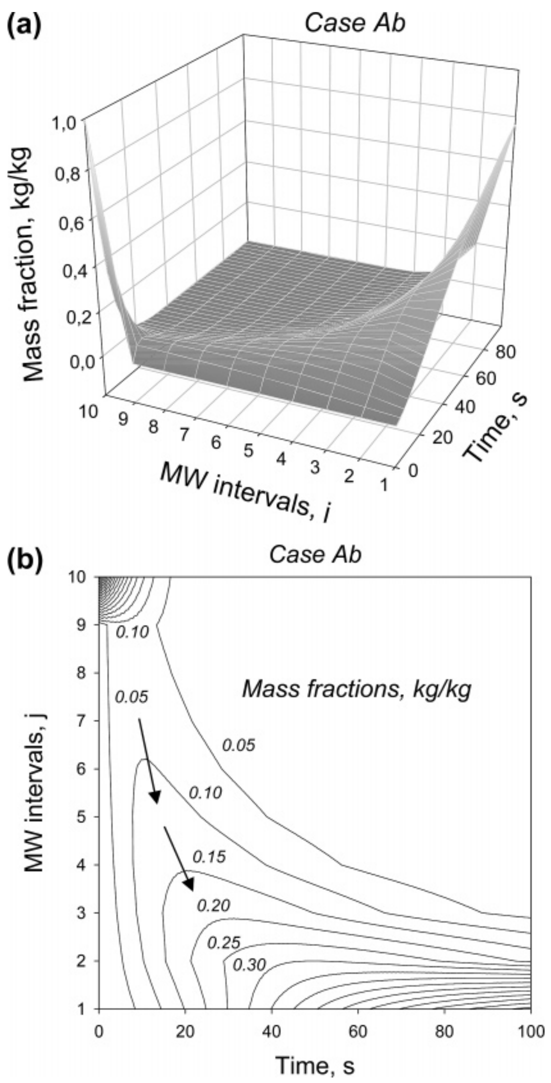

Figure 8. Evolution of MWD in case Ab.

splitting using the same scale as was applied to define the 10 MW intervals. Namely: position j means that splitting takes place after the jth segment of the molecule; therefore the resultant fragments are transferred to the intervals M_j and M_{i-j}, respectively. The other horizontal axis on the right side shows the initial MW intervals of the splitting molecules (M_i).

Data columns parallel to the front axis give the splitting probabilities at different positions j ($1 \leq j < i$) along the length of molecules in given initial MW intervals ($2 \leq i \leq 10$). Note that the maximal value of splitting positions j decreases with decreasing molecule size i, because j should be less than i. Data columns on the left side (indicated as "total") show the change of the degradation probabilities ${}_nP_i$ as a function of the initial size of molecules.

Figure 3 gives the splitting probabilities for case Ab, where ${}_nP_{j,i}$ did not change along the length of molecules, but the degradation probability ${}_nP_i$ decreased linearly with decreasing molecular weight. The maximal value of this latter was ${}_nP_{10} = 1.8 \times 10^{-2}\ \mathrm{s}^{-1}$ and diminished to ${}_nP_2 = 0.2 \times 10^{-2}\ \mathrm{s}^{-1}$. For the sake of comparison, the mean degradation probability averaged in interval $2 \leq i \leq 10$ was constant (${}_n\bar{P}_i = 1.0$) in all cases shown in Table 1.

Figure 4 shows the model parameters in case Bc, when the probability of degradation decreased exponentially with decreasing i from a value of ${}_nP_{10} = 3 \times 10^{-2}$, and splitting occurs preferentially around the middle of molecules, with decreasing probability toward the both ends, similar to a normal distribution function. Figure 5 shows the parameters used for case Cc, where the degradation probability also decreased exponentially, but splitting is most probable toward the ends of molecules. Note that these data refer to the number of splits, which differ from the mass fraction transition probabilities of matrix P. Therefore, these data were converted by eq 5 to mass fraction transitions $P_{i,j}$ resulted in asymmetric distribution along intervals M_j as is seen in Figure 6 for case Ac as an example.

Simulations with different transition probability profiles were carried out for all cases shown in Table 1, using the ModelMaker 3.0.2 software (Cherwell Scientific Publishing Ltd.).

Results and Discussion

The most interesting results are shown in Figures 7−11 as examples. Surface and contour plots in Figure 7a,b show the time evolution of molecular weight distribution obtained for case Aa. It is seen that just after the start of degradation a sudden concentration drop takes place between the intervals $j = 10$ and $j = 9$. Later on, after a nearly constant level (see the arrow on Figure 7b), the mass fractions in the successive M_j intervals are increasing gradually from $j = 5$ to $j = 2$. After 40−60 s, the mass fractions in the medium MW intervals (from $j = 7$ to $j = 3$) became almost zero, illustrated by the flat surface. Toward the smallest MW intervals (from $j = 2$ to $j = 1$) a steep rise is

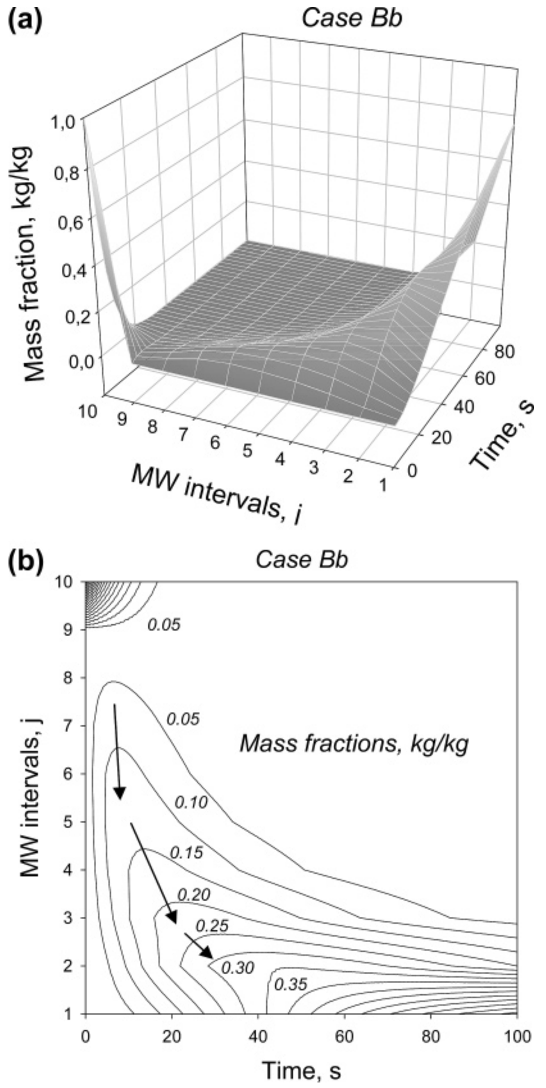

Figure 9. Evolution of MWD in case Bb.

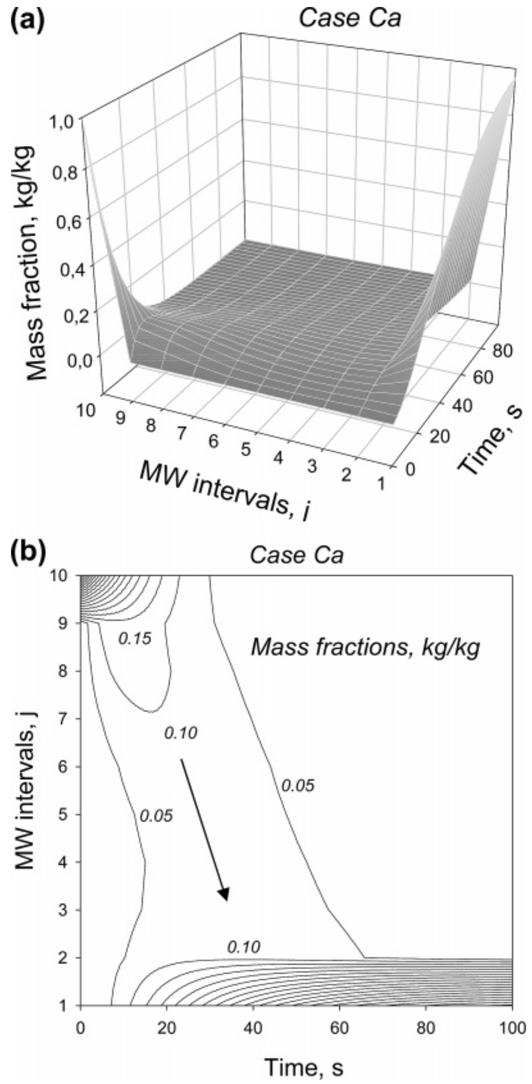

Figure 10. Evolution of MWD in case Ca.

seen at any time after 20 s. This behavior seen in this diagram is the consequence of the constant degradation probabilities for each M_i (not seen among the diagrams), which corresponds to increasing split probabilities per splitting positions when the size of the molecules diminishes. This unrealistic assumption resulted in very low accumulation in the intermediate MW regions even in the first period of process.

Figures 8 and 9 show quite different distributions: supposing linear decrease of degradation probabilities with decreasing molecular size (cases Ab and Bb) means increasing barrier against transition from higher MW intervals toward the lower ones. Therefore, the increasing accumulation of material in MW ranges from $j = 8$ to $j = 1$ appears as a continually rising ridge in a considerable time period (see the arrows on Figure 8b). Although Figures 8 and 9 are quite similar to each other, some differences can be recognized: when the split probabilities are increasing toward the center of molecules (case Bb, Figure 9); the rise of concentration along j is somewhat steeper compared to Figure 8 (case Ab—i.e., uniform probability along the length). This behavior is understandable considering that in case Bb more molecule fragments are produced with medium lengths between $j = 7$ and $j = 3$ in the first period of the process.

As regards the consequence of increasing split probability toward the ends of molecules, Figures 10 and 11 (cases Ca and Cc) reveal interesting behavior. At the beginning, considerable mass transition takes place from the highest interval ($i = 10$) to the next few ($j = 9-7$) and to the lowest MW ranges ($j = 1-2$). Therefore, the mass fractions are increasing rapidly in these lateral intervals and somewhat slower in the medium MW intervals, resulting in a concave region on the slowly rising ridge. For decreasing degradation probabilities with decreasing size (case Cc, Figure 11), the most pronounced accumulation of degradation products in the intermediate MW intervals caused a steeper rise during a longer period of the process. The mentioned concave region can be recognized even here, especially between $j = 6$ and $j = 4$ (at $t = 20-40$ s).

These diagrams have confirmed that the distribution of split probabilities along the length of molecules and the dependence on the size of the splitting molecules have characteristic influence on the evolution of molecular weight distribution of the products. This behavior can help us to identify the mechanism of degradation by evaluating the experimental data, as will be shown in the second part of this study.

As was mentioned, the model allows any kind of division along the studied molecular weight range to define MW intervals. The results discussed above were obtained with 10 uniform MW intervals. In the second part of this study, five MW intervals were used with exponentially decreasing spans to determine the transition and degradation probabilities from experimental data.

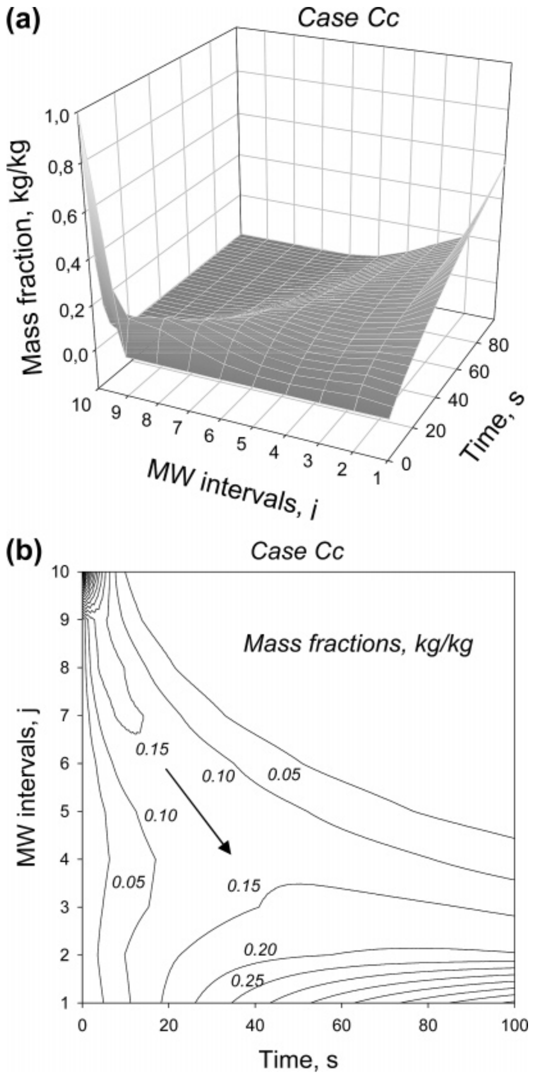

Figure 11. Evolution of MWD in case Cc.

Summary and Conclusions

A Markov-chain stochastic model was developed to investigate the effect of different split probability distributions along the length of molecules on the evolution of molecular weight distribution of the products. The number degradation probability of molecules was defined as the sum of split probabilities at different positions of a molecule. Its dependence on the molecular weight of the splitting molecules was also considered. An equation was proposed for the conversion of split probabilities to mass fraction transitions between different molecular weight fractions. To characterize the molecular weight distribution during the process, 10 discrete molecular weight intervals were defined with uniform widths along the whole MW range of the studied reaction system, supposing transitions between them, due to the fragmentation of molecules.

After principal considerations, a Markov-chain model consisted of a mass fraction transition probability matrix and a state probability vector was proposed. The time evolution of the expectable molecular weight distributions were determined by solving a set of differential equations.

The behavior of the model was investigated by supposing different split probability profiles along the length of molecules (uniform, increasing toward the middle, increasing toward the ends), also depending on the size of the splitting molecules. Simulations were carried out with nine different parameter sets resulting in characteristic molecular weight distribution profiles, which seemed to be suitable to identify the mechanism and kinetics of degradation.

Nomenclature

M_i = ith molecular weight interval, characterized by its average molecular weight, Da
m_k = mass of a splitting molecule, kg
m_l, m_m = mass of the fragments obtained by splitting of a molecule, kg
x_i = mass fraction of the material in the ith interval, relative to the total mass of material, kg/kg
Δx_i = change of mass fraction in the ith molecular weight interval during Δt time step, kg/kg
${}_nP_i$ = number degradation probability of a molecule in the ith interval during Δt time step, s^{-1}
${}_nP_{j,i}$ = split probability resulting in fragments transferred from the ith to the jth interval, s^{-1}
$P_{j,i}$ = probability of mass fraction transition from the ith to the jth interval, dimensionless (eqs 9−10), or s^{-1} (eqs 11−12)
$p(t_n)$ = state probability vector after the nth time step, eq 7
$p_i(t_n)$ = state probability or expected mass fraction in MW interval i after the nth time step, kg/kg
$p_i(t)$, $p_i(t)$ = state probability or expected mass fraction in MW intervals i or k at time t, kg/kg
P = mass transition probability matrix, eq 9
t, t_n = time, and time after the nth time step, s
Δt = time step, s

Acknowledgment

The authors acknowledge the financial support of the Hungarian National Research and Development Program (Grant NKFP 2001-3/072).

Literature Cited

(1) Dencs, J.; Nos, G.; Dencs, B.; Marton, G. Investigation of Solid-Phase Starch Modification Reactions. *Trans IchemE* **2003**, *81* (Part A), 1−5.

(2) Meiczinger, M.; Dencs, J.; Marton, G.; Dencs, B. Investigation of Reactions Occurring at Starch Phosphorylation. *Ind. Eng. Chem. Res.* **2005**, *44* (25), 9581−9585.

(3) Mehl, M.; Marongiu, A.; Faravelli, T.; Bozzano, G.; Dente, M.; Ranzi, E. A kinetic modeling study of the thermal degradation of halogenated polymers. *J. Anal. Appl. Pyrolysis* **2004**, *72* (2), 253−272.

(4) Marongiu, A.; Faravelli, T.; Bozzano, G.; Dente, M.; Ranzi, E. Thermal degradation of poly(vinyl chloride). *J. Anal. Appl. Pyrolysis* **2003**, *70* (2), 519−553.

(5) Staggs, J. E. J. Modelling random scission of linear polymers. *Polym. Degrad. Stab.* **2002**, *76*, 37−44.

(6) Staggs, J. E. J. Modelling end-chain scission and recombination of linear polymers. *Polym. Degrad. Stab.* **2004**, *85* (2), 759−767.

(7) Kostoglou, M. Mathematical analysis of polymer degradation with chain-end scission. *Chem. Eng. Sci.* **2000**, *55* (13), 2507−2513.

(8) Madras, G.; Smith, J. M.; McCoy, B. J. Degradation of Poly(methyl methacrylate) in Solution. *Ind. Eng. Chem. Res.* **1996**, *35* (6), 1795−1800.

(9) Madras, G.; Chung, G. Y.; Smith, J. M.; McCoy, B. J. Molecular Weight Effect on the Dynamics of Polystyrene Degradation. *Ind. Eng. Chem. Res.* **1997**, *36* (6), 2019−2024.

(10) Platkowski, K.; Reichert, K. H. Application of Monte Carlo methods for modelling of polymerization reactions. *Polymer* **1999**, *40* (4), 1057−1066.

(11) Ziff, R. M.; McGrady, E. D. Kinetics of polymer degradation. *Macromolecules* **1986**, *19*, 2513−2519.

(12) Galina, H.; Lechowicz, J. B. An Algorithm for Monte Carlo Modeling of Degradation of Polymer Networks. *Comput. Chem.* **1998**, *22* (1), 39−41.

(13) Emsley, A. M.; Heywood, R. J. Computer modelling of the degradation of linear polymers. *Polym. Degrad. Stab.* **1995**, *49* (1), 145−149.

(14) Nassar, R.; Chou, S. T.; Fan, L. T. Stochastic analysis of stepwise cellulose degradation. *Chem. Eng. Sci*. **1991**, *46* (7), 1651−1657.

(15) Inoue, I.; Yamaguchi, K. Particle Motion in a Mixer. Mixing in a Two Dimensional V-Type Mixer. *Int. Chem. Eng.* **1970**, *10* (3), 490−497.

(16) Wang, R. H.; Fan, L. T. Stochastic Modeling of Segregation in a Motionless Mixer. *Chem. Eng. Sci*. **1977**, *32* (7), 695−701.

(17) Gyenis, J.; Kátai, F. Determination and randomness in mixing of particulate solids. *Chem. Eng. Sci*. **1990**, *45* (9), 2843−2855.

(18) Berthiaux, H.; Mizonov, V.; Zhukov, V. Application of the theory of Markov chains to model different processes in particle technology. *Powder Technol.* **2005**, *157* (1−3), 128−137.

(19) Duggirala, S. K.; Fan, L. T. Stochastic analysis of attrition−a general cell model. *Powder Technol.* **1989**, *57* (1), 1−20.

(20) Berthiaux, H. Analysis of grinding processes by Markov chains. *Chem. Eng. Sci*. **2000**, *55* (19), 4117−4127.

Received for review October 24, 2006
Revised manuscript received September 4, 2007
Accepted September 7, 2007

IE061365G