Abstract

This paper presents a kinetic model for the calculation of polymer chain sequence length distribution in a multi-component step-growth polymerization toward the synthesis of bisphenol A co-polycarbonate. The polymerization system consists of three different types of monomers with two kinds of reactive end groups (e.g. A = phenyl carbonate group, B = hydroxyl group), AR_1A, BR_2B, and BR_3B. The kinetic model for melt polycondensation is also extended to a solid state polymerization (SSP). Simulation results show that the reactivity ratio of end groups, the condensate removal rate, particle size, and end group mole ratio have significant effects on the monomer sequence length distribution.

Key words

Sequence length distribution (SLD), polycarbonate (PC), condensation polymerization, solid-state polymerization (SSP)

Introduction

In a step-growth or condensation polymerization process, a small amount of third monomer is often added into a linear homopolymer to modify the polymer properties by changing the copolymer composition and chain sequence distribution. For a free radical polymerization process, statistical and numerical methods are well developed to calculate such chain structures.\(^1\),\(^2\) But these methods are not directly applicable to a step-growth copolymerization process. Unlike in free radical polymerization, no polymer chain is dead or inactive in condensation polymerization as long as reactive end groups are present in the reaction mixture. The previous modeling work includes a sequence length distribution model developed by Peebles \(^3\), an in-out recursive probability model developed by Lopez-Serrano \(^4\) and a linkage moment model developed Beers \(^1\). However, none of these models has taken unbalanced stoichiometric conditions into consideration and no study has been reported for a solid-state polymerization (SSP) that is used industrially to manufacture high molecular weight condensation polymers such as polycarbonate (PC), poly(ethylene terephthalate) (PET) and nylons. The rate of SSP and the polymer molecular weight are strongly dependent on the stoichiometric ratio of reactive end groups \(^5\). Although SSP has been studied in the past, little has been reported on the sequence length distribution during the SSP of a copolymer. In this work, the effects of end group mole ratio and the relative reactivities of functional end groups on the sequence length distribution are investigated.

Model development

For a linear copolymer derived from AR_1A, BR_2B, and BR_3B monomers, the molecular species are defined as shown in Table 1.
Table 1. Types of polymer molecular structure and chain length distribution

<table>
<thead>
<tr>
<th>No.</th>
<th>Molecular structure</th>
<th>Chain length distribution</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>AR₁-----R₂-----R₁-----R₂-----R₁A</td>
<td>$C_{n-i}^{-1}(1-p_1)^2 p_1^{n-1} \left(\frac{p_2}{1+v}\right)^i \left(\frac{vp_3}{1+v}\right)^{n-1-i}$</td>
</tr>
<tr>
<td></td>
<td>i units n units n-1-i units</td>
<td>$1-2p_i + p_i \frac{1+v}{p_2 + vp_3}$</td>
</tr>
<tr>
<td>2</td>
<td>AR₁-----R₂-----R₁-----R₂B</td>
<td>$2C_{n-i}^{-1}(1-p_1)^i p_1^n \left(\frac{p_2}{1+v}\right)^i \left(\frac{vp_3}{1+v}\right)^{n-1-i}$</td>
</tr>
<tr>
<td></td>
<td>i+1 units n units n-1-i units</td>
<td>$1-2p_i + p_i \frac{1+v}{p_2 + vp_3}$</td>
</tr>
<tr>
<td>3</td>
<td>AR₁-----R₂-----R₁-----R₂B</td>
<td>$2C_{n-i}^{-1}(1-p_1)^i p_1^n \left(\frac{p_2}{1+v}\right)^i \left(\frac{vp_3}{1+v}\right)^{n-1-i}$</td>
</tr>
<tr>
<td></td>
<td>i units n units n-i units</td>
<td>$1-2p_i + p_i \frac{1+v}{p_2 + vp_3}$</td>
</tr>
<tr>
<td>4</td>
<td>BR₂-----R₂-----R₁-----R₂B</td>
<td>$C_{n-i}^{-1} p_1^{n+1} \left(\frac{p_2}{1+v}\right)^i \left(\frac{vp_3}{1+v}\right)^{n-1-i} \left(\frac{1-p_2}{1+v}\right)^2$</td>
</tr>
<tr>
<td></td>
<td>i+2 units n units n-1-i units</td>
<td>$1-2p_i + p_i \frac{1+v}{p_2 + vp_3}$</td>
</tr>
<tr>
<td>5</td>
<td>BR₃-----R₂-----R₁-----R₃B</td>
<td>$C_{n-i}^{-1} p_1^{n+1} \left(\frac{p_2}{1+v}\right)^i \left(\frac{vp_3}{1+v}\right)^{n-1-i} \left(\frac{1-p_3}{1+v}\right)^2$</td>
</tr>
<tr>
<td></td>
<td>i units n units n-i+1 units</td>
<td>$1-2p_i + p_i \frac{1+v}{p_2 + vp_3}$</td>
</tr>
<tr>
<td>6</td>
<td>BR₂-----R₂-----R₁-----R₃B</td>
<td>$2C_{n-i}^{-1} p_1^{n+1} \left(\frac{p_2}{1+v}\right)^i \left(\frac{vp_3}{1+v}\right)^{n-1-i} \left(\frac{1-p_2p_3}{1+v}\right)^2$</td>
</tr>
<tr>
<td></td>
<td>i+1 units n units n-i units</td>
<td>$1-2p_i + p_i \frac{1+v}{p_2 + vp_3}$</td>
</tr>
</tbody>
</table>

Note: $p_1$, $p_2$, and $p_3$ stand for conversions with respect to each monomer, and $v$ means the initial ratio between monomer BR₂B and monomer BR₃B before reaction, and $C_{n-i}^{-1} = \frac{(n-1)!}{i!(n-1-i)!}$ (The original work was given by Case [6], but some corrections are made here).

A polymer chain in this system can be expressed as $-R₁(R₂/R₃)R₁(R₂/R₃)R₁(R₂/R₃)-$. For sequence length distribution as we follow the definition given by Lopez-Serrano [4]. For example, the sequence length of $R₂$ for the polymeric chain $-(R₂R₁R₂R₁R₂R₁)-$ is 3 and that of $R₃$ is 2 for the chain $-(R₃R₁R₃R₁)-$. It’s obvious that the $R₂$ or $R₃$ is always followed by $R₁$. If we assign ”$R₂$” as a numeric number “0” and ”$R₃$” as “1”, the backbone of a polymeric chain can be simplified as a combination of “0” and “1”. In other words, if we know the type of a chain, a
certain combination of “0” and “1” stands for a unique chain. For instance, a binary number “0000011” means the backbone of that chain is “R₂R₁R₂R₁R₂R₁R₂R₁R₂R₁R₂R₁R₃R₁”, and sequence length for “R₂” is 5 and sequence length for “R₃” is 2. If we switch the order of “0” and “1”, the binary number “0000011” can vary into “01100110”, which has 2 counts of sequence length of 1 for “R₂”, and 1 count of sequence length of 2 for “R₂” and 2 counts of sequence length of 2 for “R₃”. For a given binary number with the number of digits of “n”, and the number of “0” of “i”, the sequence length for “R₂” can be “1”, “2”, ..., “j”, ..., “i”. If polymer chains follow the most probable distribution, theoretically, the pattern of total counts for each sequence length can be found and given in the following Table 2.

<table>
<thead>
<tr>
<th>i = 1</th>
<th>i = 2</th>
<th>i = 3</th>
<th>⋯</th>
<th>i = i</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. ( nC^0_{n-2} )</td>
<td>1. ((n-1)C^1_{n-2})</td>
<td>1. ((n-2)C^2_{n-2})</td>
<td>⋯</td>
<td>1. ((n-i+1)C^{i-1}_{n-2})</td>
</tr>
<tr>
<td>2. ((n-1)C^0_{n-3})</td>
<td>2. ((n-2)C^1_{n-3})</td>
<td>⋯</td>
<td>2. ((n-i+1)C^{i-2}_{n-3})</td>
<td></td>
</tr>
<tr>
<td>3. ((n-2)C^0_{n-4})</td>
<td>⋯</td>
<td>3. ((n-i+1)C^{i-3}_{n-4})</td>
<td>⋯</td>
<td></td>
</tr>
<tr>
<td>⋯</td>
<td>j. ((n-i+1)C^{i-j}_{n-j-1})</td>
<td>⋯</td>
<td></td>
<td></td>
</tr>
<tr>
<td>i. ((n-i+1)C^0_{n-i-1})</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

where \( i \) (\( i < n \)).

From Table 2, the normalized number- and weight-average sequence distributions can be obtained. On the other hand, the chain length distribution in number average has been given in Table 1. In order to calculate the fraction of sequence length of \( j \) (\( j \geq 1 \)), we need to summate all the contributions from chain length \( n \) (\( j < n \)). Therefore, a general equation for sequence length distribution can be written as,

\[
\text{Number fraction of sequence length of } j = \sum_{m=1}^{6} \sum_{n=j+1}^{\infty} \sum_{i=j}^{n-1} \left( P_{m,n-i,j} SN_{n-1,i,j} \right)
\]

(1)

where \( P \) is the number-average chain length distribution (Table 1) and the subscripts m, n, and i represent chain types, total chain length, and number “0” (“R₂”) respectively. SN is the normalized number-average sequence distribution (normalized from Table 2).

Similarly, the weight-fraction of sequence length of \( j \) can be calculated:

\[
\text{Weight fraction of sequence length of } j = \sum_{m=1}^{6} \sum_{n=j+1}^{\infty} \sum_{i=j}^{n-1} \left( W_{m,n-i,j} SW_{n-1,i,j} \right)
\]

(2)

where \( W \) is for the weight-average chain length distribution, and SW is the normalized weight-average sequence distribution (normalized from Table 2). The weight-average chain length distribution can be calculated from the number-average chain length using the following equation.
\[ W_{m,n,i} = \frac{w_{m,n,i} P_{m,n,i}}{\sum_{n=1}^{\infty} \sum_{i=0}^{\infty} (w_{m,n,i} P_{m,n,i})} \]  

where \( w \) is the molecular weight of species.

Therefore, as long as the conversion of each monomer and the initial mole ratio between \( BR_3B \) and \( BR_2B \) are known, the sequence length distribution can be calculated using the above equations. In a melt condensation polymerization, usually there is no nonuniformity at the end of reaction and only one sequence distribution can be found. But in a SSP, the gradient of end groups may be present inside a particle, making the conversion nonuniformity grow from one layer to another. Thus, the sequence distribution near the center of a polymer particle can also be different from that at the particle surface.

In the following, we use diphenyl carbonate (DPC, AR1A), bisphenol A (BPA, BR2B) and 3,3',5,5'-tetramethylbisphenol A (TMBPA, CR2C) polymerization as an example. The prepolymer precursor can be obtained by dissolving two oligomers, bisphenol A polycarbonate (BPA-PC) and 3,3',5,5'-tetramethylbisphenol A polycarbonate (TMBPA-PC), together in chloroform and then partially crystallized in acetone liquid. We assume that the following polycondensation occurs in the amorphous phase without any side reactions.

\[
\begin{align*}
E_A + HO &\xrightarrow{k_1} OCO - C - CH_3 \\
E_B &\xrightarrow{k_1'} OH \\
E_A + HO &\xrightarrow{k_2} OCO - C - CH_3 \\
E_B' &\xrightarrow{k_2'} OH \\

\end{align*}
\]

where \( E_A = \text{phenyl carbonate group}, \ E_B = \text{hydroxyl end group from BPA}, \ E_B' = \text{hydroxyl end group from TMBPA}, \ Z = \text{polymer repeating unit}, \ \text{and} \ P = \text{phenol}. \) The kinetic model equations for \( [P], [E_B] \) and \( [E_B'] \) take the similar forms as in our previous work and initial conditions can be determined by back calculation method that have been shown in our previous work \([5]\).

**Results and discussion**

The partial differential equations in the SSP model have been solved using a parabolic PDE solver in MATLAB. The model parameters are given in Table 3.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Unit</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>( k_1 = k_r + k_i [C^+] )</td>
<td></td>
<td>[7]</td>
</tr>
</tbody>
</table>
Diffusivity of phenol: $D_p = 3 \times 10^{-8}$ cm²·sec⁻¹

Particle diameter = 0.3 mm

Degree of polymerization of BPA-PC: $\bar{X}_{n,0} = 10$

Degree of polymerization of TMBPA-PC: $\bar{X}_{n,0} = 10$

End group mole ratio in BPA-PC, $r_1'$: 1.0

End group mole ratio in TMBPA-PC, $r_2'$: 1.0

Initial mole ratio of EB/EB' = 0.1

Crystallinity change: $dx_c/dt = k_c (x_{max} - x_c)$

$k_c = 6.27 \times 10^{-4}$ min⁻¹

$x_{max} = 0.62$

Initial crystallinity: 18.3 %

Note: Regarding the forward and backward reaction rate constants for the reversible reaction between Eₐ and Eₐ', we don't have values available. Therefore, we estimate the values of $k_2$ and $k_2'$ from the reactivity ratios, $k_2/k_1$ and $k_2'/k_1'$, and treat them as adjustable parameters. As the first approximation, the equilibrium constants may be regarded as same for both cases. Then both forward reactions and backward reactions may have same reactivity ratios, $k_2/k_1 = k_2'/k_1'$. Thus, only one adjustable parameter is necessary.

Figure 1 shows the weight-average sequence length distribution calculated by the model with the parameters in Table 3. We can see that the sequence distribution of R₂ becomes broader as SSP proceeds, indicating that more R₂ are incorporated into polymer chains than R₃. For the same reactivity ratios, higher concentration of Eₐ than Eₐ' results in more R₂ incorporation. Figure 2 shows the sequence distributions at different positions in a particle at reaction time of 12 hours. For a relatively big particle, the diffusion of phenol inside
of polymer matrix is the major resistance to polymerization. As a result, the particle surface and center have the highest and the lowest reaction rate, respectively. Therefore, the conversion at the particle surface is higher than in the particle interior, and the sequence length distribution becomes broader than those in the particle.

Figure 1. Weight-average sequence distribution of $R_2$ during SSP

Figure 2. Weight-average sequence distribution of $R_2$ at $t=12$ hrs

Figure 3 shows the effect of reactivity ratio on the sequence length. Note that there is only a slight difference for different reactivity ratios ($k_1=$constant). In fact, the conversion of the third monomer in a prepolymer is 90% and the initial mole ratio of $E_B/E_B$ is 0.1. Therefore, the incorporation of $R_3$ is not significant even at higher reaction rates. Because $R_2$ is dominant in
the chain composition, and $k_1$ is constant, it has a little effect on the sequence length distribution of $R_2$. If $k_2$ is kept constant, the reaction rate difference of $k_1$ will lead to a big difference in sequence distribution of $R_2$, as shown in Figure 4.

Figure 3. The effect of reactivity ratio ($k_1'/k_1$, $k_1=$constant)

Figure 4. The effect of reactivity ratio ($k_1/k_1'$, $k_1'=constant$)

Figure 5 shows the effect of particle size. Notice that the reaction rate decreases with the increase in particle size. The sequence length distribution expected to become broad as we decrease the particle size.
Figure 5. The effect of particle size

Figure 6 shows the effect of end group mole ratio in oligomers of BPA-PC and TMBPA-PC. The stoichiometric imbalance gives rise to lower reaction rate and low conversion. Hence, better stoichiometric balance in oligomers results in broader distribution.

Figure 6. The effect of stoichiometric imbalance

References


