

# Reactive Flash Simulation of the Continuous Melt Transesterification Process of Polycarbonate\*

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**Abstract** A model of the continuous melt transesterification process of bisphenol-A and diphenyl carbonate in a continuous stirred tank reactor to produce polycarbonate is presented. The model is developed by using the molecular species model of polycarbonate melt polycondensation and the modeling method of reactive flash. Liquid phase is treated as perfect mixed flow and the vapor phase is assumed following the ideal gas law. With this model, the continuous melt transesterification process of bisphenol-A and diphenyl carbonate is examined with respect to different process parameters.

**Keywords** continuous melt transesterification, polycarbonate, simulation, continuous stirred tank reactor

## 1 INTRODUCTION

Bisphenol A polycarbonate is a very important engineering thermoplastic, which has excellent mechanical properties such as impact resistance, excellent heat resistance, transparency and other properties. It has conventionally been manufactured by the interfacial phosgenation of bisphenol-A (BPA) with phosgene and the method of an ester interchange or transesterification process with BPA and diphenyl carbonate (DPC) in melt. Although the product qualities can be controlled easily, the interfacial phosgenation method using high toxic phosgene and a great deal of organic solvents brings many environmental problems. The melt transesterification method is environment benign and it takes advantages of lower cost over the interfacial phosgenation method.

Melt transesterification is a reversible reaction and the reaction byproduct (phenol) must be removed by vacuum to obtain high molecular weight polymer. Typical melt transesterification process includes several stages under different conditions, respectively for transesterification and condensation polymerization. By comparison, the continuous melt transesterification process[1—3] to produce polycarbonate is a better choice than the batch melt transesterification. Although the melt transesterification of BPA and DPC has been studied widely[4—7], open literature on the continuous melt transesterification process to produce polycarbonate is scarce and the modeling of continuous melt transesterification process of polycarbonate has not been reported. Present publications are focused on the continuous polycondensation process[8,9]. This paper describes the simulation of the continuous melt transesterification of BPA and DPC in a continuous stirred tank reactor (CSTR) by reactive flash modeling.

## 2 CONTINUOUS TRANSESTERIFICATION PROCESS

Illustration for analysis of a continuous melt transesterification process in a CSTR is shown in

Fig.1. Feed is pumped into the reactor continuously; reaction takes place only in the liquid phase, reaction byproduct is removed by vacuum.

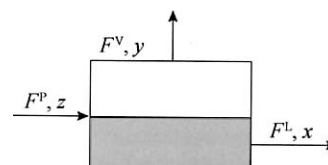
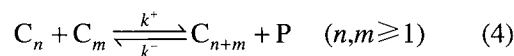
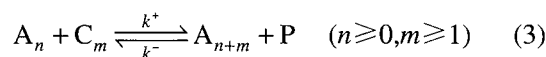
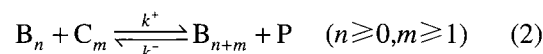
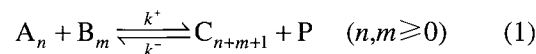


Figure 1 Illustration of reactive flash of continuous transesterification of BPA and DPC

## 3 REACTIVE FLASH MODEL FOR THE PROCESS

Either a functional group or a molecular species model can be used to model the melt transesterification process of BPA and DPC[6]. Because of the evaporation of DPC, the molecular species model is more convenient to account for this effect in modeling of the continuous melt transesterification process. Without regard to side reactions, melt transesterification of BPA and DPC can be expressed as follows:



where symbols are listed in Table 1. Note that  $A_0$  is BPA and  $B_0$  is DPC.

The reaction mixture contains mainly BPA, DPC, phenol and three kinds of oligomers with different end groups. Assuming that the reactivity of functional groups does not rely on the polymer chain length[10], reactive flash model equations can be developed as follows.

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Table 1 Symbols in reactions (1)–(4)

$A_n$	
$B_n$	
$C_n$	
P	

### 3.1 Materials balance equations

In steady state of reaction, materials balance equations can be written as

$$F^P z_{A_0} - F^L x_{A_0} + R_{A_0} = 0 \quad (5)$$

$$F^P z_{B_0} - F^V y_{B_0} - F^L x_{B_0} + R_{B_0} = 0 \quad (6)$$

$$F^P z_P - F^V y_P - F^L x_P + R_P = 0 \quad (7)$$

$$F^P z_{A_n} - F^L x_{A_n} + R_{A_n} = 0 \quad (8)$$

$$F^P z_{B_n} - F^L x_{B_n} + R_{B_n} = 0 \quad (9)$$

$$F^P z_{C_n} - F^L x_{C_n} + R_{C_n} = 0 \quad (10)$$

Symbols are defined in the nomenclature.

Total number of moles of reaction mixture can be expressed as

$$M_t = N_{A_0} + N_{B_0} + N_P + \sum_{n=1}^{\infty} N_{A_n} + \sum_{n=1}^{\infty} N_{B_n} + \sum_{n=1}^{\infty} N_{C_n} \quad (11)$$

Molar fraction of  $i$ th species in the mixture is

$$x_i = \frac{N_i}{M_t} \quad (12)$$

Generation rates of species by transesterification are[5]

$$R_{A_0} = \frac{1}{V} \left\{ -2k^+ N_{A_0} \left[ 2N_{B_0} + \sum_{n=1}^{\infty} (2N_{B_n} + N_{C_n}) \right] + k^- N_P \sum_{n=1}^{\infty} (2N_{A_n} + N_{C_n}) \right\} \quad (13)$$

$$R_{B_0} = \frac{1}{V} \left\{ -2k^+ N_{B_0} \left[ 2N_{A_0} + \sum_{n=1}^{\infty} (2N_{A_n} + N_{C_n}) \right] + k^- N_P \sum_{n=1}^{\infty} (2N_{B_n} + N_{C_n}) \right\} \quad (14)$$

$$R_P = \frac{1}{V} \left\{ k^+ \left[ 4 \left( N_{A_0} + \sum_{n=1}^{\infty} N_{A_n} \right) \left( N_{B_0} + \sum_{n=1}^{\infty} N_{B_n} \right) + \right. \right.$$

$$\left. \left. 2 \sum_{n=1}^{\infty} N_{C_n} \left[ \left( N_{A_0} + \sum_{m=1}^{\infty} N_{A_m} \right) + \left( N_{B_0} + \sum_{m=1}^{\infty} N_{B_m} \right) \right] + \left( \sum_{n=1}^{\infty} N_{C_n} \right)^2 \right\} - k^- N_P \left[ \sum_{n=1}^{\infty} (2nN_{A_n} + 2nN_{B_n} + nN_{C_n}) + \sum_{n=1}^{\infty} (n-1)N_{C_n} \right] \quad (15)$$

$$R_{A_n} = \frac{1}{V} \left\{ 2k^+ \left[ -2N_{A_n} N_{B_0} - N_{A_n} \sum_{m=1}^{\infty} (2N_{B_m} + N_{C_m}) + \sum_{r=1}^n N_{A_{n-r}} N_{C_r} \right] + k^- N_P \left[ \sum_{r=n+1}^{\infty} (N_{C_r} + 2N_{A_r}) - 2nN_{A_n} \right] \right\}, \quad (n \geq 1) \quad (16)$$

$$R_{B_n} = \frac{1}{V} \left\{ 2k^+ \left[ -2N_{B_n} N_{A_0} - N_{B_n} \sum_{m=1}^{\infty} (2N_{A_m} + N_{C_m}) + \sum_{r=1}^n N_{B_{n-r}} N_{C_r} \right] + k^- N_P \left[ \sum_{r=n+1}^{\infty} (N_{C_r} + 2N_{B_r}) - 2nN_{B_n} \right] \right\}, \quad (n \geq 1) \quad (17)$$

$$R_{C_n} = \frac{1}{V} \left\{ 2k^+ \left[ 2 \sum_{r=0}^{n-1} N_{A_{n-r}} N_{B_r} - (N_{A_0} + N_{B_0}) N_{C_n} - N_{C_n} \sum_{m=1}^{\infty} (N_{A_m} + N_{B_m} + N_{C_m}) + \frac{1}{2} \sum_{r=1}^{n-1} N_{C_r} N_{C_{n-r}} \right] + k^- N_P \left[ -(2n-1)N_{C_n} + 2 \sum_{r=n}^{\infty} (N_{A_r} + N_{B_r}) + \right. \right.$$

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