Korean J. Chem. Eng., **15**(6), 671-677 (1998)

TWO PHASE MASS TRANSFER MODEL FOR THE SEMIBATCH MELT POLYMERIZATION PROCESS OF POLYCARBONATE

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(*Received 17 August 1998 • accepted 4 November 1998*)

Abstract – A two-phase mass transfer model has been developed to predict the polymer molecular weight for the semibatch melt polymerization process of polycarbonate, in which the reaction melt viscosity is high and the mass transfer of volatile by-product is the rate-controlling step. The model simulation results have been compared with the experimental data reported in the published literature regarding the number average molecular weight and the reaction product composition. The mass transfer coefficient for phenol $[(k_La)_P]$ in the melt polymerization process of polycarbonate has been estimated.

Key words : Mass Transfer Resistance, Mass Transfer Coefficient, Vapor-Liquid Equilibrium, Polycarbonate, Melt Polymerization

INTRODUCTION

In a reversible polycondensation process, volatile condensation by-products are removed from the reaction medium by means of a vacuum applied to facilitate a forward chain growth reaction and thus to obtain high molecular weight of polymer. As the reaction proceeds the viscosity of the reaction medium increases significantly, making the removal of by-product difficult. In the melt polycondensation of diphenyl carbonate (DPC) with bisphenol-A (BPA) to produce polycarbonate, volatile reaction by-products (phenol) form bubbles in the melt phase and pass through the melt phase to a reactor head space. As phenol is produced by the reaction, it diffuses to the liquid-gas interface. The gas phase may consist of bubbles of phenol vapor and reactor head space. In the earlier stage of melt polycondensation of BPA and DPC, the reaction mass resembles a boiling liquid and the reaction mixture can be well mixed. Then phenol produced by the reaction is fully exposed to vapor phase in this stage of reaction. Therefore, the whole liquid phase can be assumed to be at equilibrium with a vapor phase in the beginning of the melt polycondensation reaction, in which the reaction process is kinetically controlled. Kim and Choi [1993] presented a vapor-liquid equilibrium model to explain the experimental data for the multistage polycondensation of BPA and DPC to polycarbonate. They used the flash calculation method to estimate the compositions and the evaporation rates of volatiles in the vapor and liquid phase. However, if phenol gas bubbles are formed in the later stage of polycondensation, there will be a certain interfacial mass transfer resistance, and the overall process becomes mass transfer controlled.

Rafler et al. [1985], who proposed a four parameter reaction-mass transport model for the melt polycondensation of polyethylene terephthalate (PET), estimated mass transfer coefficients of volatile species for varying reaction conditions. They also reported several interesting facts concerning the mass transfer process. First, a swarm of stable bubbles is formed in the stirred reactor and the total mass transfer area increases considerably. Second, the interfacial mass transfer area depends on the reactivity of the reactants (e.g., a type of the catalyst used). Third, the effective mass transfer coefficient decreases with increasing reactor pressure. Lastly, the proposed four-parameter model satisfactorily explains the experimental data. Laubriet et al. [1991] proposed a two phase mass transfer model to quantify the effect of the mass transfer process on the performance of a continuous final stage melt PET reactor. In the modeling of a screw-type finishing polycondensation reactor for PET, they found that the mass transfer limitations affect the polymer molecular weight and the concentrations of end groups and side products. They also stated that a rational way of estimating the mass transfer parameter for various reactor configurations and operating conditions, such as shaft rotational speed, melt viscosity, melt hold-up, and agitator geometry, should be developed.

The mass transfer process is represented by the model using a volumetric mass transfer coefficient, which is the product (i.e., k_La) of the mass transfer coefficient, k_L, and the interfacial area per unit volume, a. There have also been many attempts to correlate the parameter of k_La with physicochemical properties of the system (viscosity, surface tension, density, and diffusivity) and reactor operating parameters (impeller diameter, impeller speed and agitation power input) [e.g., Kawase and Moo-Young, 1988; Chaudhari et al., 1987]. Ramachandran and Chaudhari [1983] compiled many empirical correlations for the gas-liquid volumetric mass transfer coefficient (k_La). There are several reports on the measurement of volumetric mass transfer coefficients by utilizing a dynamic physical absorption technique. Ledakowicz et al. [1984] proposed an isochoric method to measure k_La in a stirred autoclave reactor, in which a pressure drop is monitored under the constant volume condition.

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They claimed that for accurate data to be obtained, the whole autoclave reactor system including the connecting lines must be kept at the same temperature.

Rafler et al. [1985] reported the values of mass transfer coefficients (k_L) and specific contact surface area (a) in the melt polycondensation of PET by using a four-parameter reaction-mass transport model. In a stirred reactor of 3.6 liter size, a typical value of k_La is 6.1×10^{-2} sec^{-1} at 280 °C and 0.45 mmHg. Ravindranath and Mashelkar [1982] also reported the value of k_La for a turbine-agitated PET reactor with the degree of polymerization of 30 to be about 1.0×10^{-2} sec^{-1}.

In this paper, a two phase mass transfer model using the volumetric mass transfer coefficient (k_La) has been applied to the multistage of polycondensation of BPA and DPC to produce polycarbonate. The value of k_La for each semibatch reaction stage is estimated based on the experimental data. Also model predictions for the multistage melt polycarbonate polymerization process predicted by both vapor-liquid equilibrium model and two phase mass transfer model are compared to each other.

MODEL DEVELOPMENT

There is no mass transfer resistance across the vapor-liquid interface at the beginning of the melt polymerization process, in which the condensation by-products (e.g., phenol) are produced in large quantity and they leave the liquid phase in large bubbles. The liquid viscosity is not high in this stage. However, as the liquid viscosity increases with conversion, the rate of phenol removal becomes a rate-controlling process. A two phase mass transfer model would be more appropriate in describing the later stage of the melt polymerization process at relatively high conversion.

A mass transfer rate of the volatiles from the liquid phase to the vapor phase is described via an effective mass transfer coefficient (k_L) and the specific interfacial contact area (a; cm^2/cm^3). The parameter a can be interpreted as a characteristic of a given reactor geometry and the melt flow distribution pattern in the reactor. As the number of bubbles in the liquid phase increases, it will contribute to an increase of the specific interfacial contact area.

The following assumptions have been made throughout the modeling of mass transfer process.

(1) Reaction (i.e., polymerization) occurs only in the liquid phase.

(2) The composition in the bulk liquid phase is uniform.

(3) Mass transfer of the volatiles at the gas-liquid interface is based on the two film model [Sherwood et al., 1975].

(4) Mass transfer resistance in the vapor film side of the interface is negligible.

(5) Only phenol and DPC vaporize during the reaction; however, BPA and polymer do not vaporize.

(6) Phenol is completely distilled off. The partial amount of DPC evaporated is refluxed back to the liquid phase. The rectification efficiency factor (ϕ) is introduced to quantify the partial loss of DPC.

(7) The interfacial concentrations of the volatiles are determined by the Flory-Huggins equation [Prausnitz, 1969].

(8) The ratio of the mass transfer coefficient of DPC to that of phenol is proportional to the ratio of the saturated vapor pressure of DPC ($P^o_{B_0}$) to that of phenol (P^o_P) at given temperature. Therefore, the volumetric mass transfer coefficient of DPC [$(k_La)_{B_0}$] is determined by that of phenol [$(k_La)_P$] given, i.e.,

$$(k_L a)_{B_0} = (k_L a)_P \cdot \frac{P^o_{B_0}}{P^o_P} \tag{1}$$

Fig. 1 shows the difference between the two-phase mass transfer model and the vapor-liquid equilibrium model in the gas-liquid interface. If the mass transfer coefficient of volatile species is sufficiently large [which is a large value of $(k_La)_P$], no concentration gradient of the species is developed in the liquid film. Therefore, a two-phase mass transfer model approaches a vapor-liquid equilibrium model when a vigorous mass transfer of volatile species occurs.

The melt polycondensation of BPA and DPC is represented by the following sequence of reactions [Kim et al., 1992]:

$$A_n + B_m \underset{k/K_{eq}}{\overset{k}{\rightleftarrows}} C_{n+m+1} + P \qquad n, m \geq 0$$

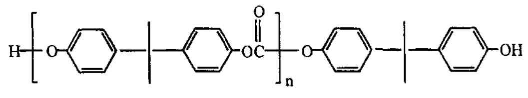
$$B_n + C_m \underset{k/K_{eq}}{\overset{k}{\rightleftarrows}} B_{n+m} + P \qquad n \geq 0,\ m \geq 1$$

$$A_n + C_m \underset{k/K_{eq}}{\overset{k}{\rightleftarrows}} A_{n+m} + P \qquad n \geq 0,\ m \geq 1$$

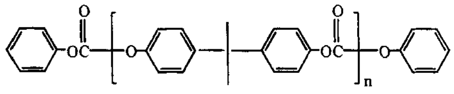
$$C_n + C_m \underset{k/K_{eq}}{\overset{k}{\rightleftarrows}} C_{n+m} + P \qquad n, m \geq 1$$

where P is phenol and the three polymeric species (A_n, B_n, and C_n) are defined as follows:

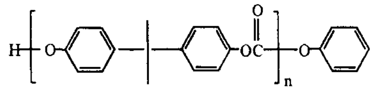
$A_n \Rightarrow$



$B_n \Rightarrow$



$C_n \Rightarrow$



Mass balances for the semibatch melt polycondensation of BPA and DPC based on the two phase mass transfer model are presented as follows:

<ins>Liquid Phase</ins>

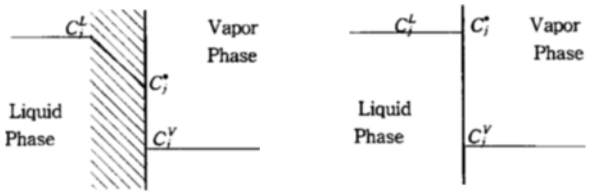
$$\frac{d[A_0]}{dt} = -\frac{[A_0]}{V}\frac{dV}{dt} + R_{A_0} \tag{2}$$

$$\frac{d[B_0]}{dt} = -\frac{[B_0]}{V}\frac{dV}{dt} + R_{B_0} - (1-\phi)(k_L a)_{B_0}([B_0] - [B_0]^*) \tag{3}$$

$$\frac{d[P]}{dt} = -\frac{[P]}{V}\frac{dV}{dt} + R_P - (k_L a)^P([P] - [P]^*) \tag{4}$$

$$\frac{d[A_n]}{dt} = -\frac{[A_n]}{V}\frac{dV}{dt} + R_{A_n} \quad (n \geq 1) \tag{5}$$

$$\frac{d[B_n]}{dt} = -\frac{[B_n]}{V}\frac{dV}{dt} + R_{B_n} \quad (n \geq 1) \tag{6}$$



(a). Mass Transfer Resistance Model (b). Vapor-Liquid Equilibrium Model

Fig. 1. Graphical representation of two process models in the gas-liquid interface for the polycarbonate melt polymerization process.

$$\frac{d[C_n]}{dt} = -\frac{[C_n]}{V}\frac{dV}{dt} + R_{C_n} \quad (n \geq 1) \tag{7}$$

where R_j is the reaction rate for each component represented as follows:

$$R_{A_0} = -2k[A_0]\{2[B_0] + \sum_{n=1}^{\infty}(2[B_n] + [C_n])\} + k'[P]\sum_{n=1}^{\infty}(2[A_n] + [C_n]) \tag{8}$$

$$R_{B_0} = -2k[B_0]\{2[A_0] + \sum_{n=1}^{\infty}(2[A_n] + [C_n])\} + k'[P]\sum_{n=1}^{\infty}(2[B_n] + [C_n]) \tag{9}$$

$$\begin{aligned} R_P = {} & k[4([A_0] + \sum_{n=1}^{\infty}[A_n])([B_0] + \sum_{n=1}^{\infty}[B_n]) + 2\sum_{n=1}^{\infty}[C_n]\{([A_0] \\ & + \sum_{m=1}^{\infty}[A_m]) + ([B_0] + \sum_{m=1}^{\infty}[B_m])\} + (\sum_{n=1}^{\infty}[C_n])^2] \\ & - k'P\{\sum_{n=1}^{\infty}(2n[A_n] + 2n[B_n] + n[C_n]) + \sum_{n=2}^{\infty}(n-1)[C_n]\} \end{aligned} \tag{10}$$

$$\begin{aligned} R_{A_n} = {} & 2k\{-2[A_n][B_0] - [A_n]\sum_{m=1}^{\infty}(2[B_m] + [C_m]) + \sum_{r=1}^{n}[A_{n-r}][C_r]\} \\ & + k'P\{\sum_{r=n+1}^{\infty}([C_r] + 2[A_r]) - 2n[A_n]\} \quad (n \geq 1) \end{aligned} \tag{11}$$

$$\begin{aligned} R_{B_n} = {} & 2k\{-2[B_n][A_0] - [B_n]\sum_{m=1}^{\infty}(2[A_m] + [C_m]) + \sum_{r=1}^{n}[B_{n-r}][C_r]\} \\ & + k'P\{\sum_{r=n+1}^{\infty}([C_r] + 2[B_r]) - 2n[B_n]\} \quad (n \geq 1) \end{aligned} \tag{12}$$

$$\begin{aligned} R_{C_n} = {} & 2k\{2\sum_{r=0}^{n-1}[A_{n-r-1}][B_r] - ([A_0] + [B_0])[C_n] \\ & - [C_n]\sum_{m=1}^{\infty}([A_m] + [B_m] + [C_m]) + \frac{1}{2}\sum_{r=1}^{n-1}[C_r][C_{n-r}]\} \\ & + k'P\{-(2n-1)[C_n] + 2\sum_{r=n}^{\infty}([A_r] + [B_r]) \\ & + 2\sum_{r=n+1}^{\infty}[C_r]\} \qquad (n \geq 1) \end{aligned} \tag{13}$$

Vapor Phase

$$\frac{d[B_0]^V}{dt} = \frac{1}{V_g}\left[[B_0]^V\frac{dV}{dt} + V(k_L a)_{B_0}([B_0] - [B_0]^*) - Q_r[B_0]^V\right] \tag{14}$$

$$\frac{d[P]^V}{dt} = \frac{1}{V_g}\left[[P]^V\frac{dV}{dt} + V(k_L a)_P([P] - [P]^*) - Q_r[P]^V\right] \tag{15}$$

The volume change of the liquid phase is expressed as

$$\begin{aligned} \frac{dV}{dt} = {} & -(1-\phi)(k_L a)_{B_0}([B_0] - [B_0]^*)V\hat{v}_{B_0} \\ & - (k_L a)_P([P] - [P]^*)V\hat{v}_P \end{aligned} \tag{16}$$

In mass balances for liquid and vapor phase, $[\cdot]$ is the molar concentrations, $[\cdot]^*$ the equilibrium concentration at the gas-liquid interface and Q_r the volumetric flow rate of vapor from the reactor. $\hat{v}_{B_0}$ and $\hat{v}_P$ are the molar volume of DPC and phenol in the liquid phase. The superscript V denotes the vapor phase and V_g the vapor phase volume.

In the development of the two-phase mass transfer model, it is assumed that the reaction temperature is constant and the reactor pressure (p_t) is also kept constant. Since the ideal gas law is assumed for the vapor phase, the following equation holds:

$$\frac{d}{dt}([P]^V + [B_0]^V) = 0 \tag{17}$$

Then, from Eqs. (14) and (15) we obtain

$$\begin{aligned} & ([P]^V + [B_0]^V)\frac{dV}{dt} + V(k_L a)_P([P] - [P]^*) \\ & + V(k_L a)_{B_0}([B_0] - [B_0]^*) - Q_r([P]^V + [B_0]^V) = 0 \end{aligned} \tag{18}$$

Note that $([P]^V + [B_0]^V) = p_t/RT$. Using Eqs. (16) and (18), we can obtain the following expression for the volumetric vapor flow rate from the reactor to the distillation column:

$$\begin{aligned} Q_r = {} & V(k_L a)_{B_0}([B_0] - [B_0]^*)\left[\frac{RT}{p_t} - (1-\phi)\hat{v}_{B_0}\right] \\ & + V(k_L a)_P([P] - [P]^*)\left[\frac{RT}{p_t} - \hat{v}_P\right] \end{aligned} \tag{19}$$

The average molecular weights of polymer ($\overline{M}_n$ & $\overline{M}_w$) are computed by using the following molecular weight moment equations.

$$\lambda_{A,k} = \sum_{n=1}^{\infty} n^k A_n \quad \lambda_{B,k} = \sum_{n=1}^{\infty} n^k B_n \quad \lambda_{C,k} = \sum_{n=1}^{\infty} n^k C_n \tag{20}$$

$$\lambda_{i,3} = \frac{\lambda_{i,2}(2\lambda_{i,2}\lambda_{i,0} - \lambda_{i,1}^2)}{\lambda_{i,1}\lambda_{i,0}} \quad (i = A,\ B,\ C) \tag{21}$$

$$\overline{M}_n = \frac{\sum_{n=1}^{\infty}(A_n w_{A_n} + B_n w_{B_n} + C_n w_{C_n})}{\sum_{n=1}^{\infty}(A_n + B_n + C_n)} = \frac{S_1}{S_0} \tag{22}$$

$$\overline{M}_w = \frac{\sum_{n=1}^{\infty}(A_n w_{A_n}^2 + B_n w_{B_n}^2 + C_n w_{C_n}^2)}{\sum_{n=1}^{\infty}(A_n w_{A_n} + B_n w_{B_n} + C_n w_{C_n})} = \frac{S_2}{S_1} \tag{23}$$

where

$$S_0 = \lambda_{A_0} + \lambda_{B_0} + \lambda_{C_0}$$

$$\begin{aligned} S_1 = {} & (254.3)(\lambda_{A_1} + \lambda_{B_1} + \lambda_{C_1}) + (228.29)\lambda_{A_0} + (214.22)\lambda_{B_0} \\ & + (94.11)\lambda_{C_0} \end{aligned}$$

$$\begin{aligned} S_2 = {} & (254.3)^2(\lambda_{A_2} + \lambda_{B_2} + \lambda_{C_2}) + (2)(254.3)[(228.29)\lambda_{A_1} \\ & + (214.22)\lambda_{B_1} + (94.11)\lambda_{C_1}] + (214.22)^2\lambda_{B_0} + (94.11)^2\lambda_{C_0} \end{aligned}$$

$$w_{A_n} = (254.3)n + 228.29\ ;\quad w_{B_n} = (254.3)n + 214.22\ ;$$
$$w_{C_n} = (254.3)n + 94.11$$

The forward and reverse reaction rate constants (k & k') used in this model are the effective rate constants in which the catalyst concentration effect is incorporated, i.e., $k=\underline{k}\cdot(N^*/V)$, $k'=\underline{k}'\cdot(N^*/V)$ where N^* is the number of moles of catalyst added. The kinetic parameters for $\underline{k}$ and $\underline{k}'$ were reported by Kim et al. [1992].

The total number of moles of DPC ($n^C_{B_0}$) and phenol (n^C_P) being removed from the reactor is calculated from the following equations:

$$\frac{dn^C_{B_0}}{dt} = (1-\phi)Q_r[B_0]^V \tag{24}$$

$$\frac{dn^C_P}{dt} = Q_r[P]^V \tag{25}$$

The interfacial equilibrium concentrations of volatile species are calculated by using the Flory-Huggins equation. The partial pressure of the volatile species j in the vapor phase is expressed as

$$p_j = p_t y_j = \gamma_j p^o_j x_j \tag{26}$$

where y_j and x_j are the mole fractions of component j in the vapor phase and the liquid phase, respectively, γ_j the activity coefficient, p^o_j the saturated vapor pressure and p_t the reactor pressure.

Assuming that the ratio of molar volumes of polymers to volatiles in the liquid phase is much larger than 1.0 (m_j>>1) and that the concentrations of volatiles are very low [$(1-\Phi_j) \rightarrow 1$], we can reduce the Flory-Huggins equation to the following form [Ravindranath and Mashelkar, 1982]:

$$\gamma_j \simeq (1/m_j)\exp(1+\chi_j) \tag{27}$$

where χ_j is the polymer-solvent interaction parameter. The volume fraction of component j in the liquid phase (Φ_j) can be approximately expressed as

$$\Phi_j \simeq \frac{x_j}{m_j} \tag{28}$$

Then, the partial pressure of phenol in the vapor phase can be expressed as

$$p_P = p_t y_P = p^o_P \frac{P\hat{v}_P}{V}\exp(1+\chi)$$
$$= p^o_P[P]^*\hat{v}_P \exp(1+\chi) \tag{29}$$

where P represents the number of moles of phenol in the liquid phase and $[P]^*$ the equilibrium molar concentration of phenol at the vapor-liquid interface. Since the ideal gas law is assumed, the equilibrium interfacial concentrations of phenol and DPC are given as

$$[P]^* = \frac{RT}{p^o_P\hat{v}_P \exp(1+\chi_P)}[P]^V \tag{30}$$

$$[B_0]^* = \frac{RT}{p^o_{B_0}\hat{v}_{B_0}\exp(1+\chi_{B_0})}[B_0]^V \tag{31}$$

Here χ_P for phenol is 0.73 and χ_{B_0} for DPC is 0.39.

RESULTS AND DISCUSSION

The two phase mass transfer model requires two unknown parameters [i.e., ϕ and $(k_La)_P$] to be estimated. The reflux efficiency factor (ϕ) for DPC was introduced to account for the imperfect distillation efficiency. A value of 1.0 for ϕ means that DPC vaporized from the reaction mixture is perfectly refluxed back to the reactor and there is no evaporative loss.

To evaluate the applicability of the two-phase mass transfer model to the description of the semibatch transesterification process, the experimental data for the five stage semibatch melt polymerization experiments presented by Kim and Choi [1993] have been utilized in this study and compared with the model predictions. The reflux efficiency factor (ϕ) estimated by Kim and Choi [1993] was also used in the mass transfer model simulations. Therefore, in the two-phase mass transfer model, the only parameter to be estimated is the mass transfer coefficient of phenol [$(k_La)_P$]. In the batch transesterification stage (i. e., Stages 1 & 2), the mass transfer of volatile species from the liquid to the vapor phase was assumed to be negligible. Table 1 and Table 2 show the reaction conditions and the estimated values of ϕ and $(k_La)_P$ in each reaction stage of the multistage polycarbonate melt polymerization process for two separate polymerization experiments (i.e., Run-I & Run-II). Stage-1 and stage-2 are the batch reaction stages pressurized slightly at 2 atm of N_2 gas; however, stage-3, stage-4, and stage-5 are the semibatch reaction stages operated below the atmospheric pressure.

A standard optimal parameter estimation technique (Rosenbrock's direct search method) [Rosenbrock, 1960] was used to estimate the optimal value of $(k_La)_P$ by minimizing the differ-

Table 1. The reaction conditions and estimated values of ϕ and $(k_La)_P$ for Run-I

Stage no.	Rxn. time (min)	Temp. (°C)	Press. (mmHg)	ϕ	$(k_La)_P$ (min^{-1})
1	0-120	180	1480	–	–
2	120-153	180 → 250	1480	–	–
3	153-273	250	150 (1 hr)	0.3	10.0
			50 (1 hr)	0.3	10.0
4	273-298	250 → 280	50	0.3	2.5
5	298-358	280	10	0	2.5
Amount of catalyst ($LiOH\cdot H_2O$) added				4.198 times 10^{-5} mol	
Initial number of moles of BPA				1.15 mol	
Initial molar ratio of DPC to BPA				1.22	

Table 2. The reaction conditions and estimated values of ϕ and $(k_La)_P$ for Run-II

Stage no.	Rxn. time (min)	Temp. (°C)	Press. (mmHg)	ϕ	$(k_La)_P$ (min^{-1})
1	0-120	230	1480	—	—
2	120-142	230 → 250	1480	—	—
3	142-262	250	150 (1 hr)	0.61	13.7
			50 (1 hr)	0.61	13.7
4	262-297	250 → 280	50	0.61	3.1
5	297-357	280	10	0	3.1
Amount of catalyst used in the reaction				4.205×10^{-5}mol	
Initial number of moles of BPA				1.31 mol	
Initial molar ratio of DPC to BPA				1.07	

ences between the experimental polymer molecular weight (i. e., number average molecular weight, $\overline{M}_n$) data and the model predictions for each stage. In this study, it was also assumed that the mass transfer coefficients for phenol in stages 4 and 5 were identical, that is, $(k_La)_{P,4}=(k_La)_{P,5}$. The estimated mass transfer coefficients for phenol in stage-3 and stage-4 are 10.0 min^{-1} and 2.5 min^{-1} for Run-I and 13.7 min^{-1} and 3.1 min^{-1} for Run-II, which have never been reported in the open literature. The reaction rate constant value based on the reaction condition for stage-3 of Run-I is 9.0 l/mol·min, and hence it shows that the polymerization is kinetically controlled up to stage-3 and after that it is mass transfer controlled.

Fig. 2 represents the comparison of $\overline{M}_n$ profiles predicted by the two-phase mass transfer model (MTR) and the vapor-liquid equilibrium model (VLE) along with the experimental observations (● symbols) for Run-I. It shows that MTR gives reasonable predictions of $\overline{M}_n$ over the entire stages with some deviations in the final stage. The $\overline{M}_n$ data observed in the final stage are closer to the MTR prediction than the VLE prediction. It should be noted that there was only one measurement in the final stage (Stage 5) of Run-I. Because the objective of the optimal parameter estimation procedure was to minimize the difference between the model prediction and the experimental data, a lack of data from 298 min to 358 min could have caused a poor estimation of the $(k_La)_P$ value. Polymer molecular weight profiles predicted by two models are almost superimposed up to stage-3; however, the two profiles deviate from each other after that.

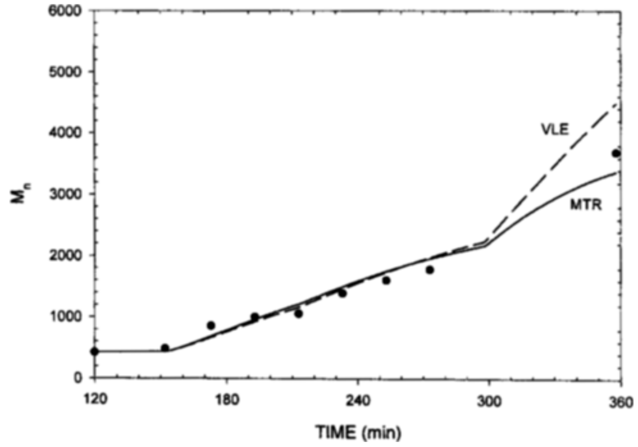


Fig. 2. Comparison of the number average polymer molecular weight profiles predicted by the two phase mass transfer model (MTR) and the vapor-liquid equilibrium model (VLE) along with the experimental observations (● symbols) for Run-I; Only the semibatch reaction stage has been presented.

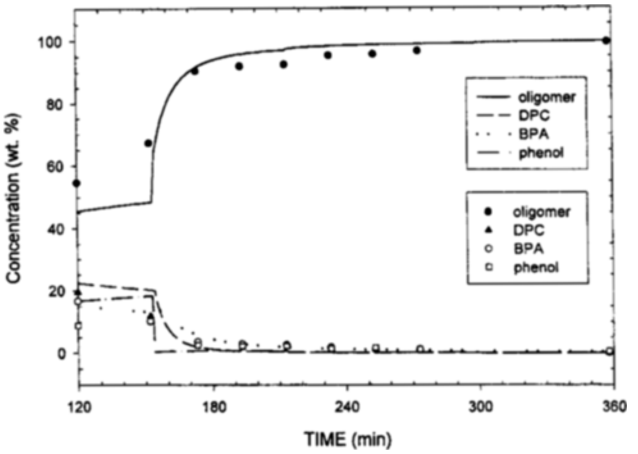


Fig. 3. Comparison of the reaction product composition profiles predicted by the two phase mass transfer model and the experimental observations for Run-I; Only the semibatch reaction stage has been presented.

Fig. 3 shows the reaction product composition profiles, experimental data (symbols) and two phase mass transfer model predictions (lines) for Run-I. Note that the agreement between the experimental data and the model predictions for concentrations (i.e., wt%) of oligomer, DPC, BPA, and phenol in stage-3 to stage-5 (semibatch reaction stage) is very good.

Fig. 4 and Fig. 5 represent $\overline{M}_n$ and the reaction product composition profiles (wt%) for Run-II, respectively. Model predictions for the reaction product composition are based on MTR. There is also good agreement between the experimental observations and the MTR predictions for $\overline{M}_n$.

Fig. 6 shows the comparison of the two model predictions for the composition profiles of oligomer and phenol for Run-I, in which the two models are MTR and VLE. The applicability of MTR as well as VLE for the prediction of the oligomer and phenol compositions is established. All the profiles presented in this study (Fig. 2 to Fig. 6) show that MTR well predicts $\overline{M}_n$ and the reaction product composition for the polycarbonate melt polymerization process operated in the semibatch fashion.

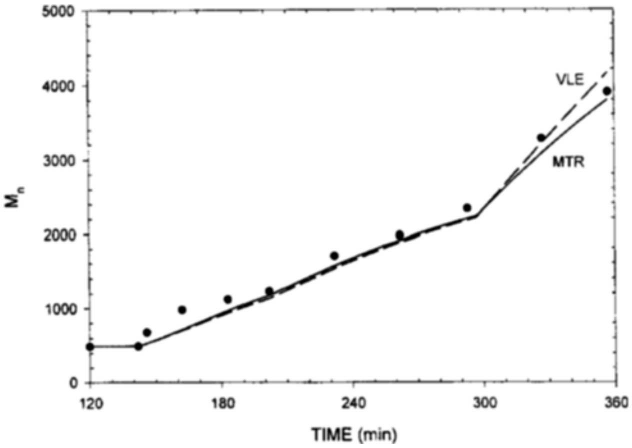


Fig. 4. Comparison of the number average polymer molecular weight profiles predicted by the two phase mass transfer model (MTR) and the vapor-liquid equilibrium model (VLE) along with the experimental observations (● symbols) for Run-II; Only the semibatch reaction stage has been presented.

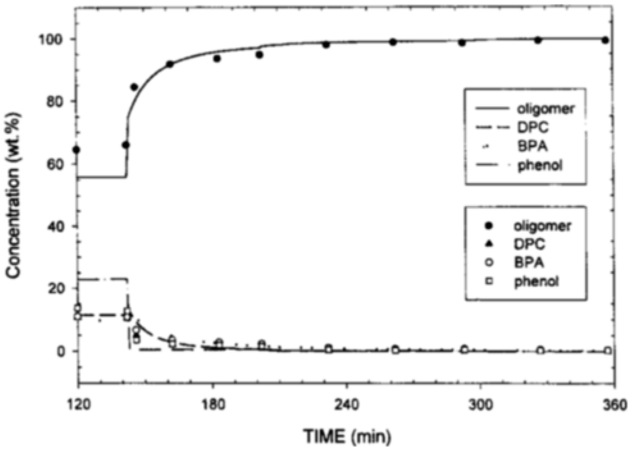


Fig. 5. Comparison of the reaction product composition profiles predicted by the two phase mass transfer model and the experimental observations for Run-II; Only the semibatch reaction stage has been presented.

Note that MTR has been presented in order to theoretically predict the semibatch polycarbonate melt polymerization process, which is operated in the mass transfer controlling state. There have been some discrepancies between the two models in the $\overline{M}_n$ predictions for the later stages of the multistage melt polymerization process of polycarbonate (stage-3 to stage-5), in which it is believed that a mass transfer of phenol from the liquid phase to the vapor phase controls the whole polymerization process. A disagreement between these two models in the mass transfer controlling stage keeps enlarged with proceeding the semibatch reaction to increase the polymer molecular weight. It should be noted that VLE does not explain the mass transfer resistance process occurring in the highly viscous reaction medium.

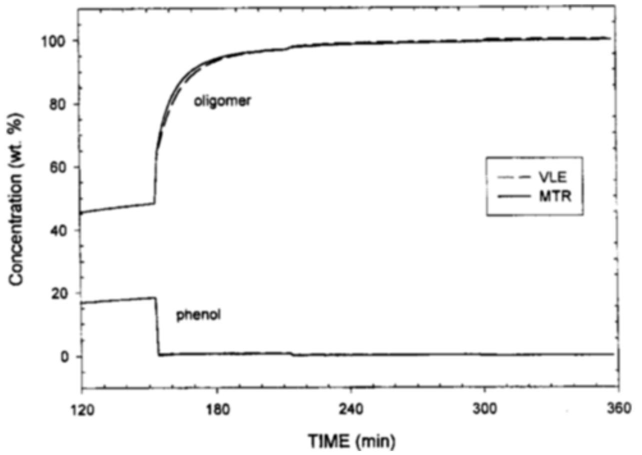


Fig. 6. Comparison of the two model predictions (VLE & MTR) for the composition profiles of oligomer and phenol for Run-I; Only the semibatch reaction stage has been presented.

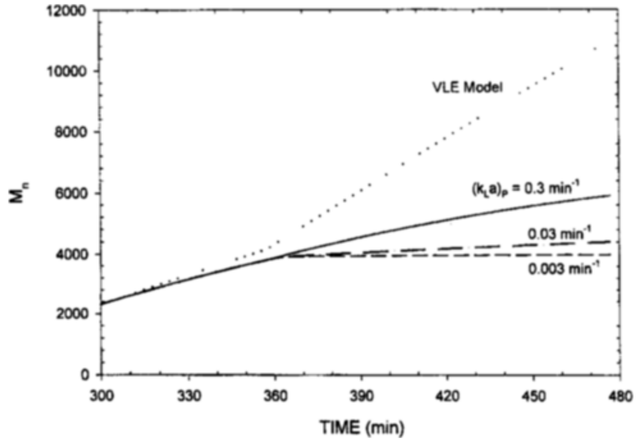


Fig. 7. Effect of the mass transfer resistance on the build-up of the polymer molecular weight in the post-stage of semibatch reaction.

Fig. 7 shows the effect of the mass transfer resistance on the build-up of $\overline{M}_n$ in a post-stage of the semibatch reaction. It has been assumed that after the end of stage-5 in Run-II, the reaction temperature is increased to 300 °C, the reaction pressure is further decreased to 1 mmHg, and the polymerization proceeds for 2 hours in addition. It is also assumed that the ϕ-value is zero because there is no remaining DPC in this stage. A decrease of the mass transfer coefficient of phenol [$(k_La)_P$], which means an increase of the mass transfer resistance, suppresses the increase of polymer molecular weight. However, the polymer molecular weight profile predicted by VLE keeps increasing with the reaction time and shows a large deviation from the model prediction by MTR.

The main theoretical background of MTR is that there is a mass transfer resistance at the gas-liquid interface. In the later stages of the semibatch melt polymerization process producing high molecular weight of polycarbonate, a reaction medium is very viscous and the mass transfer resistance increases. Such a presence of mass transfer resistance is represented by MTR. The MTR is very reliable and comprehensive in predicting the polymer molecular weight compared with VLE. In the use of MTR, two unknown parameters [ϕ and $(k_La)_P$] should be known, and they have been estimated by using the parameter estimation technique in this study. Experimental observation or theoretical analysis regarding ϕ and $(k_La)_P$ should be reported in further studies and it could make the process model comprehensive. The mass transfer coefficient is not a physicochemical property of the system, but it depends on the reactor operating conditions (e.g., efficiency of mixing, bubble size, number of bubbles, etc.). Obviously, they are not easy to measure experimentally, and this also is an important research theme to be carried out further.

CONCLUSION

A two-phase mass transfer model has been developed as an alternative modeling approach to the homogeneous vapor-liquid equilibrium model for the polycarbonate melt polymerization process. The DPC reflux efficiency factor (ϕ) estimated from the vapor-liquid equilibrium model, which has been previously reported by Kim and Choi [1993], was used in the model simulations. The mass transfer coefficient for phenol $[(k_La)_P]$ was estimated using a standard technique for optimal parameter estimation with the experimental data of number average polymer molecular weight in each stage. The model simulation results were compared with the experimental data presented by Kim and Choi [1993].

The two phase mass transfer model gives reasonable predictions of polymer molecular weight and reaction product composition. The two-phase mass transfer model is an appropriate reaction-transport model for the high conversion melt polymerization process, in which the reaction melt viscosity is high and the mass transfer of volatile by-products is the rate-controlling step. A mass transfer resistance model shows that the build-up of polymer molecular weight with reaction time is suppressed depending on the increase of mass transfer resistance of phenol, while the vapor-liquid equilibrium model does not express such a process.

To improve the two-phase mass transfer model, it is necessary to establish a theoretical procedure to estimate two parameters, ϕ and $(k_La)_P$, appearing in the model development.

ACKNOWLEDGEMENT

This work was supported by 1996 Inje University Research Grant. The author expresses sincere appreciation to Professor Kyu-Yong Choi, University of Maryland, College Park, U.S.A for his comments on this study.

NOMENCLATURE

a : interfacial area per unit volume
$(k_La)_j$: volumetric mass transfer coefficient of component j
k_L : mass transfer coefficient
p_j : partial pressure of component j
p_t : reactor pressure
P_j^o : vapor pressure of component j
Q_r : volumetric flow rate of vapor from the reactor
R_j : reaction rate for component j
$\hat{v}_j$: molar volume of component j
V : liquid phase volume
V_g : gas phase volume
x_j : mole fraction of component j in liquid phase
y_j : mole fraction of component j in vapor phase

Greek Letters

χ : polymer-solvent interaction parameter
γ : activity coefficient
ϕ : DPC reflux efficiency factor

Superscripts

C : condensate phase
V : vapor phase

Subscripts

B_0 : DPC
P : phenol

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