

KINETICS OF MELT TRANSESTERIFICATION OF BISPHENOL-A AND DIPHENYL CARBONATE TO POLYCARBONATE WITH TETRAETHYL AMMONIUM HYDROXIDE AS CATALYST

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Abstract

The catalyzed reaction kinetics of melt transesterification of diphenyl carbonate and bisphenol-A to polycarbonate has been studied in a closed system in the presence of tetraethyl ammonium hydroxide as a catalyst at the temperature range of 155-175 °C. The effects of catalyst concentration and reaction temperature on the reactants, byproduct phenol and formed oligomers have also been analyzed. Both forward and backward reaction rate constants and the equilibrium constants are determined. The enthalpy of reaction is calculated to be -20.74kJ/mol based on the Van's Hoff plot. A detailed molecular species model at a specified repeating unit has been developed and directly integrated solved. For quantification of the oligomers, the standard curves of oligomers have been reversely derived. The model values show good agreement with the experimental data.

Keywords

Polycarbonate, Melt transesterification, Tetraethyl ammonium hydroxide.

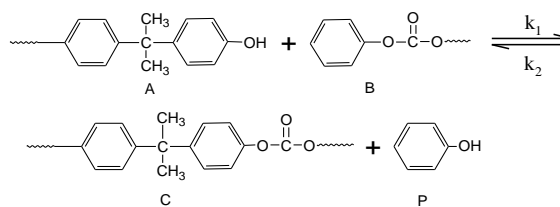
Introduction

Polycarbonate is an important thermoplastic engineering polymers with high heat resistance, impact resistance, and excellent optical clarity. The kinetics of melt transesterification of diphenyl carbonate (DPC) with bisphenol-A (BPA) to polycarbonate oligomers have been studied in the presence of tetraethyl ammonium hydroxide (TEAH) which is a more efficient transesterification catalyst than conventional alkali metal in the temperature range of 155-175 °C and ambient pressure. The effects of reaction temperature and catalyst concentration on reaction degree and oligomers formation are analyzed by HPLC (Bailey et al., 1986). Based on the functional group model, the reaction rate constant and equilibrium constant can be determined experimentally. And then, according to the obtained reaction rate constant, a modified molecular species model (Kim, 1992. Qin et al., 2006) has been developed and solved by Runge-Kutta method with the help of Matlab. The concentration changes of DPC, BPA,

phenol and oligomers have also been tracked by the molecular species model, the model calculated values show very good agreement with experimental data.

Kinetic Model

Functional Group Model



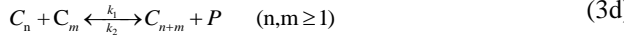
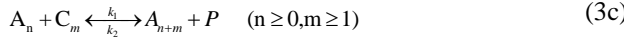
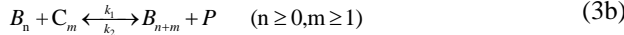
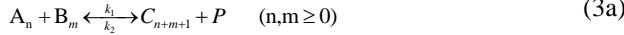
When the reactants are added at equimolar ratio, the reaction rate equation can be written as follows:

$$\frac{d[P]}{dt} = k_1 \left\{ ([A]_0 - [P])^2 - \frac{[P]^2}{K} \right\} \quad (1)$$

$$\frac{\sqrt{K}}{2[A_0]} \ln \frac{[A_0] - [P] + \frac{[P]}{\sqrt{K}}}{[A_0] - [P] - \frac{[P]}{\sqrt{K}}} = k_1 \cdot t \quad (2)$$

Molecular Species Model

Without regard to the side reactions, the melt transesterification reaction of DPC and BPA can be expressed by the following sequence of reactions:



$$\frac{dA_0}{dt} = \frac{n_{cat}}{V^2} \cdot (-4k^+ A_0 B_0 - 4k^+ A_0 (B_1 + B_2) + k^- P (C_1 + C_2 + C_3) - 2k^+ A_0 (C_1 + C_2 + C_3) + 2k^- P (A_1 + A_2 + A_3)) \quad (4)$$

$$\frac{dB_0}{dt} = \frac{n_{cat}}{V^2} \cdot (-4k^+ A_0 B_0 - 4k^+ B_0 (A_1 + A_2) + k^- P (C_1 + C_2 + C_3) - 2k^+ B_0 (C_1 + C_2 + C_3) + 2k^- P (B_1 + B_2 + B_3)) \quad (5)$$

$$\frac{dP}{dt} = \frac{n_{cat}}{V^2} \cdot (4k^+ A_0 B_0 + 4k^+ A_0 (B_1 + B_2) + 4k^+ B_0 (A_1 + A_2) + 4k^+ A_1 B_1 - k^- P (C_1 + 2C_2 + 3C_3) + 2k^+ B_0 (C_1 + C_2 + C_3) + 2k^+ (B_1 C_1 + B_1 C_2 + B_2 C_1) - 2k^- P (B_1 + 2B_2 + 3B_3) + 2k^+ A_0 (C_1 + C_2 + C_3) + 2k^+ (A_1 C_1 + A_2 C_2 + A_2 C_1) - 2k^- P (A_1 + 2A_2 + 3A_3) + k^+ (C_1 C_1 + 2C_1 C_2) - k^- P (C_2 + 2C_3)) \quad (6)$$

$$\frac{dA_1}{dt} = \frac{n_{cat}}{V^2} \cdot (-4k^+ A_1 B_0 - 4k^+ A_1 B_1 + k^- P (C_2 + C_3) - 2k^+ A_1 (C_1 + C_2) + 2k^+ A_0 C_1 - 2k^- P A_1 + 2k^- P (A_2 + A_3)) \quad (7)$$

$$\frac{dA_2}{dt} = \frac{n_{cat}}{V^2} \cdot (-4k^+ A_2 B_0 + k^- P C_3 - 2k^+ A_2 C_1 + 2k^+ A_0 C_2 + 2k^+ A_1 C_1 - 4k^- P A_2 + 2k^- P A_3) \quad (8)$$

$$\frac{dA_3}{dt} = \frac{n_{cat}}{V^2} \cdot (2k^+ A_0 C_3 + 2k^+ (A_1 C_2 + A_2 C_1) - 6k^- P A_3) \quad (9)$$

$$\frac{dB_1}{dt} = \frac{n_{cat}}{V^2} \cdot (-4k^+ B_1 A_0 - 4k^+ A_1 B_1 + k^- P (C_2 + C_3) - 2k^+ B_1 (C_1 + C_2) + 2k^+ B_0 C_1 - 2k^- P B_1 + 2k^- P (B_2 + B_3)) \quad (10)$$

$$\frac{dB_2}{dt} = \frac{n_{cat}}{V^2} \cdot (-4k^+ B_2 B_0 + k^- P C_3 - 2k^+ B_2 C_1 + 2k^+ B_0 C_2 + 2k^+ B_1 C_1 - 4k^- P B_2 + 2k^- P B_3) \quad (11)$$

$$\frac{dB_3}{dt} = \frac{n_{cat}}{V^2} \cdot (2k^+ B_0 C_3 + 2k^+ (B_1 C_2 + B_2 C_1) - 6k^- P B_3) \quad (12)$$

$$\frac{dC_1}{dt} = \frac{n_{cat}}{V^2} \cdot (4k^+ A_0 B_0 - k^- P C_1 - 2k^+ B_0 C_1 - 2k^+ C_1 (B_1 + B_2) + 2k^+ P (B_1 + B_2 + B_3) - 2k^+ A_0 C_1 - 2k^+ C_1 (A_1 + A_2) + 2k^- P (A_1 + A_2 + A_3) - 2k^+ C_1 (C_1 + C_2) + 2k^- P (C_2 + C_3)) \quad (13)$$

$$\frac{dC_2}{dt} = \frac{n_{cat}}{V^2} \cdot (4k^+ (A_0 B_1 + A_1 B_0) - 2k^- P C_2 - 2k^+ B_0 C_2 - 2k^+ C_2 B_1 + 2k^+ P (B_2 + B_3) - 2k^+ A_0 C_2 - 2k^+ C_2 A_1 + 2k^- P (A_2 + A_3) - 2k^+ C_2 C_1 + k^+ C_1 C_1 - k^- P C_2 + 2k^- P C_3) \quad (14)$$

$$\frac{dC_3}{dt} = \frac{n_{cat}}{V^2} \cdot (4k^+ (A_0 B_2 + A_1 B_1 + A_2 B_0) - 3k^- P C_3 - 2k^+ B_0 C_3 + 2k^+ P B_3 - 2k^+ A_0 C_3 + 2k^- P A_3 + 2k^+ C_1 C_2 - 2k^- P C_3) \quad (15)$$

Conclusions

The forward reaction rate constants (k^+) and the backward reaction rate constants (k^-) can be calculated according to the Eq. (2), as follows:

$$k^+ = 2.26 \times 10^{13} \exp\left(\frac{-95990}{RT}\right) \quad L^2 / mol^2 \cdot min$$

$$k^- = 7.15 \times 10^{15} \exp\left(\frac{-117048}{RT}\right) \quad L^2 / mol^2 \cdot min$$

Based on the predetermined forward (k^+) and backward (k^-) reaction rate constants, the Eq. (4)-(15) can be directly solved by the Runge-Kutta method.

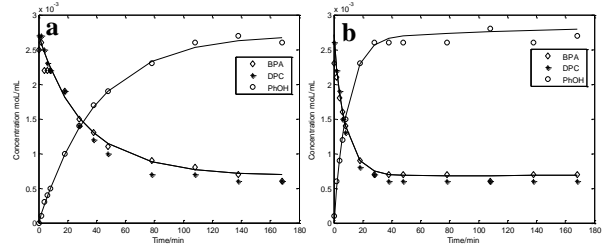


Figure 1. HPLC experimental (dot) and calculated (solid line) concentration changes of BPA, DPC and Phenol for different catalyst concentration at 165 °C. a-TEAH/BPA=1.05e-5, b-TEAH/BPA=4.34e-5.

Figure 1 displays the HPLC experimental and model calculated concentration changes of BPA, DPC and Phenol for different catalyst concentrations. It can be found that the model predictions are well agreement with the experimental data.

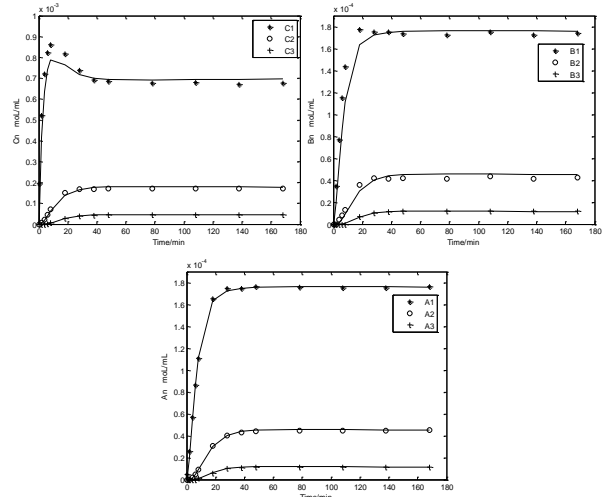


Figure 2. Oligomers concentration profiles at 165 °C. TEAH/BPA=4.34e-5

Figure 2 displays the HPLC experimental and model calculated concentration changes of oligomers. It can be found that the model predictions based on molecular species model are well agreement with the experimental data.

References

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