

Thesis Title Mathematical Modelling and Computer Simulation of  
Polymerization Reactions: The Free-Radical  
Polymerization of Styrene.

Name Wuttipong Rungseesantivanon

Degree Master of Science (Polymer Science)

Thesis Supervisory Committee

Anucha Euapermkiati, Ph.D.

Pranee Phinyocheep, Doctorat de l'Université du Maine

Preedeepon Limcharoen, Ph.D.

Date of Graduation 27 May B.E. 2537 (1994)

### ABSTRACT

The kinetics of thermal-initiated free radical polymerization of styrene (ST) in the presence of carbon tetrachloride (CCl<sub>4</sub>) or 1-butanethiol (1-BuSH) chain transfer agents (CTA) were studied experimentally and computationally in details. The deterministic dynamic predictive model of the kinetics was established. Computer programmes were written in Microsoft® Quick BASIC computer language to solve the algebraic and differential equations using the 4<sup>th</sup> order Runge-Kutta and Newton-Ralphson numerical integration methods. The modified Mayo Equation derived from the proposed kinetics was also established. Fourier-transfrom Raman spectroscopic technique was used to evaluate styrene, carbon tetrachloride and 1-butanethiol consumptions at specific reaction time. Gel Permeation Chromatography (GPC) was employed to obtain molecular weight (MW) and MW distribution (MWD) of the polymers synthesized. The overall rates of polymerization ( $R_{ST,CTA}$ ) and of loss of CTA ( $R_{CTA}$ ) had the relation to  $k'_{ST,CTA}[ST]^p[CTA]^q$  and to  $k'_{CTA}[ST]^s[CTA]^t$ , respectively, where  $k'_{ST,CTA}$  and  $k'_{CTA}$  are the apparent rate constants and p, q, s and t are the exponent order. When

CTA is  $\text{CCl}_4$ , the values of  $p$ ,  $q$ ,  $s$ ,  $t$ ,  $k'_{\text{ST,CTA}}$ , and  $k'_{\text{CTA}}$  were evaluated equal to 0.95, -0.07, 0.99, 0.91,  $4.88 \times 10^{-5}$  l/mol.s, and  $8.40 \times 10^{-7}$  l/mol.s, respectively. When CTA is 1-BuSH, the values of  $p$ ,  $q$ ,  $s$ ,  $t$ ,  $k'_{\text{ST,CTA}}$ , and  $k'_{\text{CTA}}$  were determined equal to 0.97, 0.24, 1.51, 0.38,  $1.10 \times 10^{-4}$  l/mol.s., and  $5.31 \times 10^{-5}$  l/mol.s, respectively. The simulation values of rate constant for the propagation reaction ( $k_p$ ) and that for the transfer reaction ( $k_{\text{tr}}$ ) were evaluated, and the values were used for computer simulation to predict  $M_n$ ,  $M_w$  and MWD. The experimental and simulation results of  $M_n$  and  $M_w$  are in good agreement, while those of MWD were not when CTA is 1-BuSH. The experimental and simulation chain transfer constant ( $C_x$ ) were determined from the original and modified Mayo Equations. For CTA is  $\text{CCl}_4$ ,  $C_x$  as obtained from the original Mayo Equation was  $1.06 \times 10^{-2}$  and  $6.7 \times 10^{-3}$  and as obtained from the modified Mayo Equation was  $1.07 \times 10^{-2}$  and  $6.9 \times 10^{-3}$ . For CTA is 1-BuSH,  $C_x$  obtained from the original Mayo Equation was  $4.42 \times 10^{-1}$  and  $7.61 \times 10^{-1}$  whereas that obtained from the modified Mayo Equation was 1.63 and 1.24, respectively.