

PP-I-3

FREE RADICAL THERMAL POLYMERIZATION OF STYRENE: DETERMINATION OF THE INITIATION RATE

Francisco López-Serrano R.^{*} (1), Jorge. E. Puig (2) and Jesús. Alvarez (3).

(1) DEPG FQ-UNAM flserr@hotmail.com, (2) CUCEI U. de G. puig_jorge@hotmail.com,

(3) Dpto. Hidrca. e Ing. de Procs. UAM-I. MEXICO jac@xanum.uam.mx

Summary: The old problem of styrene free radical thermal polymerization kinetic scheme is revisited, due to the fact that understanding the thermal free radical polymerization is crucial to model any high temperature polymerization reaction. Utilising an observability-based approach¹⁻³ two parameters (R_i and K_p) are determined from conversion and number average molecular weight (M_n) data⁴. Here, differently as previously done, no model assumptions are drawn on those parameters. Under the hypothesis that the third parameter (K_{tr}) can take two constant forms ($K_{tr} = \text{constant}$ or $K_{tr} = C_m K_p$ where $C_m = k_{tr}/k_p = \text{constant}$) a third measurement (M_w) is taken to verify that $K_{tr} = \text{constant}$ is the more consistent assumption. It was found that the initiation rate; R_i , presents three monomer exponent dependencies from 1.5, 0.7 and 1, and this is different as reported earlier⁴.

Methodology. The scheme used here agrees with the one obtained by Tefera⁵. Only termination by disproportion is considered. Living; λ_i and dead; μ_i moments, as well as m_0 ; the initial monomer concentration, are in moles, the nomenclature is referred elsewhere⁴. If pseudo steady state is assumed on the living radical population (λ_i) one obtains:

$$\frac{dx}{dt} = (1-x) (K_p + K_{tr}) R_i^{1/2} \quad (1)$$

$$\frac{d\mu_0}{dt} = R_i V/2 + m_0(1-x) K_{tr} R_i^{1/2} \quad (2)$$

$$\frac{d\mu_2}{dt} = \frac{R_i V [m^2 (K_p + 2K_{tr}) (3K_p + 2K_{tr}) + 2R_i V^2] + m (K_p + K_{tr}) R_i^{1/2} (m^2 K_{tr} (2K_p + K_{tr}) + 5 R_i V^2)}{[m K_{tr} + R_i^{1/2} V]^2}$$

$$m = m_0(1-x); K_p = k_p/k_t^{1/2}; K_{tr} = k_{tr}/k_t^{1/2} \quad (3)$$

From equations 1-3 it can be seen that three parameters appear: R_i , K_p and K_{tr} . Here, a combination of a standard constant-parameter with an observability-based time-varying parameter¹⁻³ was used. In an inner loop, with conversion; x and μ_0 measurements the time-varying parameters R_i and K_p were determined. The remaining parameter; K_{tr} , was considered under two possibilities. First, $C_m (= k_{tr}/k_p)$ and then K_{tr} were considered constant. These two cases were verified comparing the weight average molecular weight (M_w) model prediction and experimental data⁴ at 120°C (Fig. 2).

Results and Conclusions. The conversion and M_n estimation (not shown) exactly coincide with the experimental data. The initiation rate shows a three interval exponent behavior (1.5, 0.7 and linear, from low to high conversion) when analyzed versus monomer concentration (see Fig. 1). This result does not agree with the previous work reported by Hui and Hamielec⁴, they reported an exponent of three for the whole interval. The time-varying functional behavior of R_i and K_p were obtained without any modeling assumptions on any of those parameters. The lumped parameter $k_t/k_p^2 [= (1/K_p)^2]$ shows a continuous decay with conversion (Fig. 3), as reported earlier^{4,5}. The assumption that K_{tr} is constant appears to be more consistent than assuming that C_m is constant (see Fig. 2).

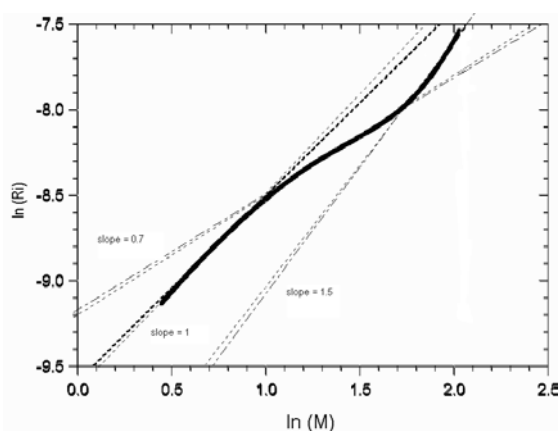


Fig. 1. Functional behavior of R_i with monomer concentration M (mol/l)

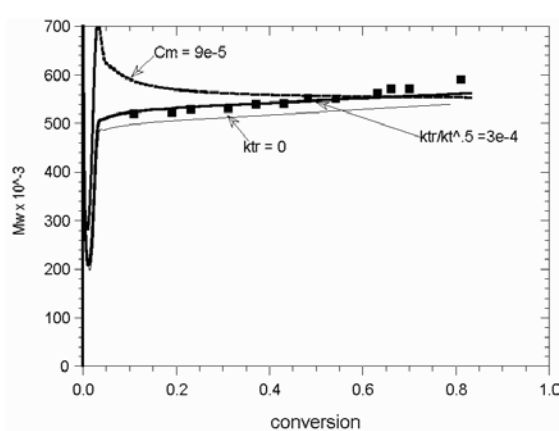


Fig. 2. M_w fitting for constant C_m and constant $k_{tr}/k_t^{1/2}$ (data from ref. 5 at 120°C)

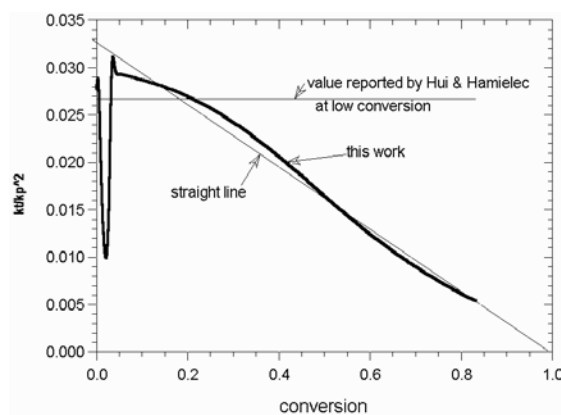


Fig. 3 Functional behavior of the lumped parameter k_t/k_p^2

References

- (1) Alvarez J. and T. López, AIChE J, Robust Dynamic State Estimation of Nonlinear Plants **45**(1), 107-122 (1999)
- (2) Alvarez, J., Journal of. Process Control."Nonlinear State Estimation with Robust Convergence", **10**, 59-71 (2000)
- (3) López-Serrano, F., J. E. Puig and J. Alvarez. Determination of Parameters In 0-1 Emulsion Polymerization. Macromol. Symp. **150**, 59-65 (2000)
- (4) Hui A. W., and A. E. Hamielec, Thermal Polymerization of Styrene at High Conversions and Temperatures. An Experimental Study. J. of Appl Poly. Sci., **16**, 749-769 (1972)
- (5) Tefera, N., G. Weickert, K. R. Westerterp. Modeling of Free Radical Polymerization up to High Conversion. I. A Method for the Selection of Models by Simultaneous Parameter Estimation. J. of Appl. Poly. Sci. **63**, 1649-1661 (1997)