

Copolymerization Reactivity Ratios Estimation: An Integro-Differential Approach

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Abstract. In this work, a combined integro-differential estimation approach is applied to find the reactivity ratios (RR) dependencies on monomer feed composition. First, an integral-based interpolation and data smoothing, followed by analytic differentiation are performed. Then, a differential method is used to obtain the RR dependency on composition. Finally the integral method-based analytic representation of the RR dependencies is obtained. The proposed sequential procedure is put in perspective with the techniques employed before, and is applied to two copolymerization systems: Para-Chloro Styrene/Styrene (PCS/STY) and PCS/ Para-Methoxy Styrene (PMOS) with composition and average propagation measurements. In all cases, the reactivity ratio pair exhibited dependency on composition, with a behavior different from the one predicted by the penultimate model. In one case (PCS/STY), the behavior resembled the one of the bootstrap model.

Introduction. In the case of free-radical copolymerizations, the most widely used tool for prediction is the terminal or Mayo-Lewis[1] model, involving two key parameters which are referred to as the reactivity ratios (RR). However, several reports indicate that this model is unable to predict the copolymerization propagation rate constants[2,3,4] in spite of describing well the copolymer composition. To address the problem, the penultimate and bootstrap[3] models, with more adjustable parameters, have been proposed. In the penultimate model case, with only composition measurements, the possibility of multiple solutions for the set of RR constants has been reported[5]. Besides composition, the bootstrap³ model testing requires the propagation rate constant measurements[6]. The method has been useful in explaining solvent effects[7]. In some cases, measures of microstructure, like sequence distribution, have been also been employed to fit and test the models[4]. The RR model testing and parameter fitting problems have been basically addressed with the nonlinear regression-based integral method combined with deterministic or statistical hypothesis testing tools[8,9,10]. In a recent study on the thermally initiated polymerization system[11], a differential estimation approach was employed to obtain the plots of the dependencies of three parameters on conversion from the mass equations in conjunction with conversion and molecular weight measurements, without needing the assumption of a particular kinetics model, at the cost of more experimental data.

Model Identification Problem. Let y and x denote monomer 1 (mole fraction) composition in the polymer and feed (composition) forms, respectively, and write the corresponding Mayo-Lewis model[1]:

$$y = \frac{r_1 x^2 + x(1-x)}{r_1 x^2 + 2x(1-x) + r_2(1-x)^2} := f(x, r_1, r_2) \quad (1)$$

where, $r_1 = k_{11}/k_{12}$, $r_2 = k_{22}/k_{21}$, r_1 and r_2 are the reactivity ratios, which are defined in terms of the homo (k_{11} and k_{22}) and the cross (k_{12} and k_{21}) propagation rate constants. The corresponding average propagation rate constant is given by

$$\langle k_p \rangle = \frac{r_1 x^2 + 2x(1-x) + r_2(1-x)^2}{r_1 x/k_{11} + r_2(1-x)/k_{22}} \quad (2)$$

Integro-Differential Method. The proposed approach has three sequential steps: i) an integral-based interpolation and data smoothing, followed by analytic differentiation, ii) the reactivity ratios determination based on a differential method, and iii) the integral method-based analytic

representation of the reactivity ratios dependencies. This sequential procedure is depicted in more detail next.

Data interpolation and derivation. Using a standard regression-based integral method, an empirical or physically-based reactivity model $h_i(x, c_i)$, with an adjustable parameter vector c_i , is fitted to the experimental data $D(p)$, yielding a smooth continuous representation

$$y(x) = \phi[x, h_i(x, c_i)] := \phi(x), \quad x \in [0, 1] \quad (3a)$$

of the experimental sequence, in the understanding that the adequacy of these continuified data, is assessed on the error reports basis and criteria provided by regression packages, like error plots, standard deviation, confidence intervals and the fitted parameters uncertainty. Then, the smooth function $\phi(x)$ (eq 7a 3) analytic differentiation yields the smooth derivative of the data plot,

$$y'(x) = \phi'(x), \quad x \in [0, 1] \quad (3b)$$

Reactivity ratios dependencies determination. Taking the differential of f defined in eq 1 and g (eq 3) is given by:

$$g(x, r) = \frac{\partial f(x, r)}{\partial x} = \frac{(1-x) + 2x(r_1 - 1)r_2 + x^2(r_1 + r_2 - 2r_1r_2)}{\{r_2 + x[2 - 2r_2 + x(r_1 + r_2 - 2)]\}^2} \quad (4)$$

r_1 and r_2 , at the given composition x , are the unknowns, and $y(x)$ and $y'(x)$, at the composition x , are the data. From standard nonlinear algebraic equation arguments follows that, for a given data pair $[x, y(x)]$, the algebraic equation pair eq 3, has a unique (possibly numerically drawn) solution

$$r_1 = \frac{(1-x)[2y(x) - y(x) + (1-x)xy'(x)]}{x\{2[1 - y(x)]y(x) - (1-x)xy'(x)\}} \quad (5a)$$

$$r_2 = \frac{x\{[3 - 2y(x)]y(x) - (1-x)xy'(x) - 1\}}{x\{2[1 - y(x)]y(x) - (1-x)xy'(x)\}} \quad (5b)$$

Provided that the following condition is met

$$\delta(x, r) = \frac{x^2(1-x)^2}{\{r_2 + x[2 - 2r_2 + x(r_1 + r_2 - 2)]\}^3} \neq 0 \quad \text{for } 0 < x < 1 \quad (6)$$

where $\delta(x, r)$ is the Jacobian matrix O determinant, associated to the equation pair 1, 4.

Reactivity ratios dependencies analytic representation. In the last step, the $r_1(x)$ and $r_2(x)$ plots, over the interval x , are examined and fitted, via the integral method application over the entire composition interval $[0, 1]$ to an adequate pair of analytic curves, preferably drawn from or connected to sound physical-chemical interpretation:

$$r = \rho(x, c_a) \quad (7)$$

where c_a is a vector of p_a parameters. By doing so, the RR functions determination can benefit from the robust integral method interpolation-filtering capability and by the differential method model assessment and discrimination capability. In general, the integro-differential method functioning depends on the experimental data number and its uncertainty as well as on the functions $y(x)$, $y'(x)$ and $\sigma(x)$ complexity. Depending on the specific case under consideration, more on the key subject of the function assessment sensitivity with respect to interpolation model parameters, as well as to data number and uncertainty will be discussed briefly on the subsequent section.

PCS/STY and PCS/PMOS Systems. The interpolation and differential estimation steps application of the proposed methodology were applied to the PCS-PMOS and the PCS-STY[12] systems at 40°C, yielding the results shown in Figure 1 and 2, respectively. As it can be seen in Figure 2, the r_{PCS} is definitely non constant for both systems, the r_{PMOS} is basically constant and r_{STY} is mildly away from a constant behavior. With regard to the analytic representation step, the penultimate model was considered, and the predictions (continuous and dashed plots) shown in the same figure were obtained with the fitted parameters. In this case, the penultimate model depicts poorly the RR evolution, especially for the r_{PCS} reactivity ratio for both systems and performs only a good description for the r_{PMOS} reactivity ratio in the PCS-PMOS system. Since the above mentioned experiments include propagation rate constant measurements with two methods size exclusion

chromatography (SEC) and size exclusion chromatography/differential viscometry (SEC/DV), in the understanding that this measurement constitutes a means to assess the modeling capability. For the same purpose, our RR functions and the homopolymerization rate constants⁵ were used to estimate the average propagation rate constant (see eq 2) presented in Figures 3 (PCS/STY) and 4 (PCS/PMOS), where the full circles represent data obtained by SEC-DV techniques and the empty circles refer to the standard SEC technique. In the same figures are presented the predictions (red plots) according to Coote and Davis[12] ultimate model and data. While the proposed (with Coote and Davis k_{11} and k_{22}) and the ultimate model approaches yield an acceptable behavior in the PCS/PMOS system (Figure 4), both approaches break down in the PCS/STY system (Figure 3).

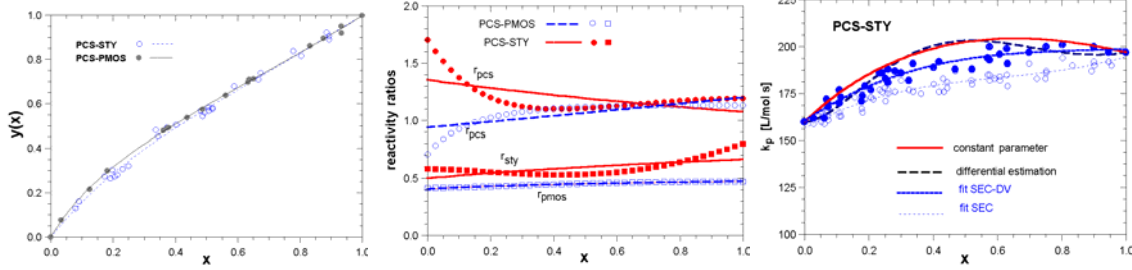


Fig.1. Polymer vs. monomer

Fig.2 RR dependencies

Fig. 3. k_p dependencies

According to the ultimate model approach, this signifies that an error exists in the reactivity and/or the propagation models, which are built under the assumption of constant RR and homopropagation constants. On the other hand, in the proposed approach the RR dependencies on composition are obtained from mass balances in conjunction with accepted kinetics assumptions (i.e., radicals in QSS and LCA), without any reactivity and propagation modeling assumptions, and this lead us to conclude that there could be a modeling error in the propagation model (i.e., with constant values of k_{11} and k_{22}).

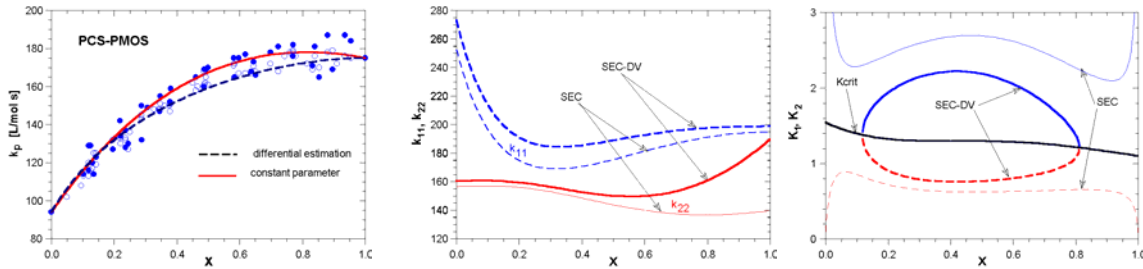


Fig.4. k_p dependencies

Fig.5. k_{ii} dependencies

Fig. 6. K_1 and K_2 vs. x

To address this issue, regard the system (PCS/STY) with the most measurement uncertainty, or equivalently, with the worst case example, and apply the differential approach to the composition and propagation constant measurements, with both the reactivity and propagation rates as functions of composition to be determined. The resulting average propagation interpolation and the homopropagation functions are presented in Figures 3 and 5, respectively. According to Figure 5: (i) both homopropagation parameters exhibit dependency on the composition, (ii) k_{11} definitely depends on composition with the same trend from different propagation determinations, and (iii) the same is true for k_{22} up to ca. 0.7 composition, and the assessment beyond this point can be improved by taking more data. In the case of having the bootstrap (quadratic in K) model with the values of r_{1p} and r_{2p} obtained with the composition data and the k_{11} and k_{22} constant values from Coote and Davis[12], the application of the proposed methodology yields the results presented in Figure 6. Since The bootstrap eq has two positive solutions over the composition interval [0.15, 0.75], two solution functions exist for the pair (k_1 , k_2) over that composition interval. Here, the observability

property with respect to the partition coefficient (K) is ill-conditioned in the composition intervals $[0, 0.15]$ and $[0.75, 1]$ as well as in a region about the curve of K_{crit} versus composition shown in Figure 6, and the system is not observable in the curve $K_{\text{crit}}(x) = \{[k_{22}/r_{1p}(x)]/[k_{11}/r_{2p}(x)]\}^{1/2}$. In this figure can be seen that the lower (or upper) solution of $K(x)$, below (or above) $K_{\text{crit}}(x)$, is slightly concave (or convex), the lower solution is nearly constant, especially for the SEC measurement case, and this means that the PCS-STY system is reasonably well described by the bootstrap model with constant equilibrium and homopropagation parameters. The existence of this two-solution feature has not been reported, perhaps because one of the roots has been disregarded by the nonlinear regressor when choosing among multiple minima, and a more conclusive discussion on the matter requires further study.

Conclusions. A combined integro-differential approach to determine the RR on monomer feed dependencies has been developed. While in the integral method the dependencies are determined after the adequate fitting of a candidate model, in the integro-differential method the dependency plots are obtained without needing any *a priori* modeling assumption, and the analytic form of the RR functions follows from a straightforward curve fitting scheme. The proposed integro-differential estimation approach, with a set of sequential steps, was put in perspective with the techniques employed before, and applied to two copolymerization systems, (PCS/STY and PCS/PMOS) with composition and average propagation measurements. In both cases, the reactivity ratio pair exhibited dependency on composition, with a behavior different from the one predicted by the penultimate model. In one case (PCS/STY), the behavior resembled the one of the bootstrap model. The possibility of a comonomer effect was detected where the RR could change due to a solvent effect caused by the other monomer concentration. Comparing with previous studies with integral method, the proposed differential approach constitutes an improvement in simplicity, systematization and modeling assessment capabilities.

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