

Fundamental Aspects of Measuring Copolymerization Reactivity Ratios Using Real-Time FTIR Monitoring

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Summary: Real-time FTIR is a powerful tool to obtain copolymerization reactivity ratios because it allows simultaneous monitoring of individual monomer consumption rates. Based on the Mayo-Lewis equation we showed that in reactivity ratios can be defined as the ratios of apparent rate constants of monomer consumption. The validity and limitations on this new method are discussed in the isobutylene-isoprene and isobutylene-styrene carbocationic copolymerization systems.

Keywords: carbocationic copolymerization; infrared spectroscopy; isobutylene; isoprene; reactivity ratios; styrene

Introduction

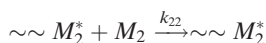
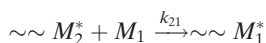
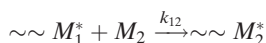
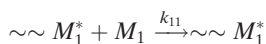
Real-time Infrared (IR) spectroscopy is a powerful tool to monitor polymerizations and associated reactions.^[1,2] This method is particularly useful for monitoring copolymerizations, because individual comonomer consumption profiles can be obtained simultaneously. The importance of copolymers should not be underestimated; for example, two thirds of the estimated 10 million metric tons of polystyrene produced commercially is used in copolymers or blends. The composition of a copolymer is determined by relative comonomer concentrations in the reaction medium and by the ratio of reactivities between the comonomers. The availability of accurate copolymerization reactivity ratios is extremely important commercially in order to control copolymer composition. Puskas et al.^[3] reported controlling copolymer composition in the commercial butyl process based on measuring the conversion of isobutylene and predicting isoprene con-

version based on the dominant reactivity ratio $r_{IB} = k_{11}/k_{12}$. This method has been working well for more than ten years and is used for statistical process monitoring and control.

This paper will discuss some fundamental aspects of reactivity ratio measurement using *real time* FTIR monitoring.

Fundamentals

The copolymerization reactivity ratios in a simple binary system (monomers 1 and 2) are defined as $r_1 = k_{11}/k_{12}$ and $r_2 = k_{22}/k_{21}$, where k_{ij} refers to rate constants of homo-propagation and k_{ij} to cross-propagation:



This model is known as the “terminal model”, because it is assumed that the reactivity of the chain ends is only influenced by terminal monomer unit, and not the penultimate unit. The Mayo-Lewis

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(M-L) differential equation for such a copolymerization system is:^[4]

$$\left(\frac{d[M_1]}{d[M_2]}\right) = \frac{[M_1](r_1[M_1] + [M_2])}{[M_2]([M_1] + r_2[M_2])} \quad (1)$$

where $[M_1]$ and $[M_2]$ are the instantaneous concentrations for monomer 1 and 2 at time t and r_1 and r_2 are their reactivity ratios, respectively. The vast majority of published reactivity ratio estimates were obtained by carrying out copolymerization experiments to low conversion with various feed compositions, analyzing the chemical composition of the copolymers and evaluating the data using linear methods such as the M-L (eq.1) or the Finemann-Ross methods.^[4,5] These methods carry inherent errors: for example, simple re-indexing (M_1 to M_2 and vice versa) may lead to different r_1 and r_2 values. Later Kelen, Tüdös and Turcsanyi (K-T)^[6,7] developed improved methods to reduce the error in r_1 and r_2 estimates and to enable evaluation of reactivity ratios using high-conversion data. Computer technology led to the development of non-linear methods.^[8] However, chemists continue to use linear methods.

In-situ monitoring of copolymerizations provides more accurate instantaneous monomer composition data than off-line methods such as gravimetric sampling and, consequently, more accurate reactivity-ratio estimates. Long *et al.* have calculated reactivity ratios from *real-time* FTIR low-conversion data for the free-radical copolymerization of acrylonitrile with methacrylate using a non-linear method,^[9] and for maleic anhydride with norbornene using a linear graphical procedure.^[10] These reports used *real-time* monitoring coupled with well established methods to analyze instantaneous composition data. Reed *et al.* used ACOMP (Automatic Continuous Monitoring of Polymerizations using a diluted side stream) with RI (Refractive Index) and UV detection to obtain instantaneous compositions and reactivity ratios in free-radical methyl methacrylate - styrene copolymerization over the whole con-

version range.^[11] Puskas *et al.* reported a high-throughput method of calculating reactivity ratios from instantaneous FTIR monomer concentrations in the carbocationic copolymerization of isobutylene (IB) with isoprene (IP).^[1] They treated each polymerization experiment as a series of “low conversion experiments” and calculated r_1 and r_2 from single experiments for any given F-G data pair:

$$r_1 = \frac{G_1 - G_2}{F_1 - F_2} \quad (2)$$

$$r_2 = r_1 F_1 - G_1 \quad (3)$$

where

$$G = \frac{X(Y-1)}{Y} = \frac{\frac{[M_1]}{[M_2]} \left(\frac{d[M_1]}{d[M_2]} - 1 \right)}{\frac{d[M_1]}{d[M_2]}} \text{ and}$$

$$F = \frac{X^2}{Y} = \frac{\frac{[M_1]^2}{[M_2]^2}}{\frac{d[M_1]}{d[M_2]}}$$

The large number of data points that can be generated in a single experiment using *in-situ* FTIR (>100) significantly reduced the error in the reactivity ratios. Both linear (M-L and K-T) and non-linear (Non-linear Least Square (NLLS) van Herk algorithm) analysis showed good agreement with predicted values of $r_1 = 1.32$ and $r_2 = 0.74$ calculated using Mayr's nucleophilicity scale.^[12,13] Combination of the K-T and NLLS methods yielded $r_1 = 1.17 \pm 0.01$ and $r_2 = 0.99 \pm 0.02$.

This paper will report the development of a new and practical method to predict copolymer composition using *real-time* FTIR monitoring.

Derivation of Reactivity Ratio Expressions Using Apparent Rate Constants

The rate of consumption of monomer 1 in the batch reactor is defined as

$$\frac{d[M_1]}{dt} = k_{1app}[M_1] \quad (4)$$

where k_{1app} is the apparent rate constant (a pseudo-kinetic rate constant).^[14] If k_{1app} is constant over a certain time interval,

equation (4) can be integrated over that interval to give:

$$\ln\left(\frac{[M_1]_0}{[M_1]}\right) = k_{1app}t \quad (5)$$

where $[M_1]_0$ is the concentration of monomer 1 at the beginning of the interval, and $[M_1]$ is the concentration t time units later. Similar equations can be written for monomer 2. As a result, apparent rate constants for the comonomers can be obtained from the slopes of semi-logarithmic rate plots obtained from FTIR monitoring. An example for IB-IP copolymerization is shown in Figures 1 and 2. Instantaneous comonomer concentrations were obtained from the areas under the FTIR bands characteristic of the $=CH_2$ wag overtone in IB at 1780 cm^{-1} , and the C–H stretch overtone in IP at 1815 cm^{-1} (Figure 1), for which proportionality with concentrations was established.^[1] (The small initial deviation from linearity after the first few points is most likely due to the temperature spike after initiation). Dividing eq. (4) by the analogous equation written for M_2 gives (for simplicity, only equations for M_1 will be given explicitly):

$$\frac{d[M_1]}{d[M_2]} = \frac{k_{1app}[M_1]}{k_{2app}[M_2]} \quad (6)$$

From eq. (5), the instantaneous monomer concentration can be expressed as:

$$[M_1] = [M_1]_0 \exp(-k_{1app}t) \quad (7)$$

Division of eq. (7) by the analogous expression for monomer 2 gives:

$$\frac{[M_1]}{[M_2]} = \frac{[M_1]_0 \exp(-k_{1app}t)}{[M_2]_0 \exp(-k_{2app}t)} = \frac{[M_1]_0}{[M_2]_0} \exp[(k_{2app} - k_{1app})t] \quad (8)$$

Substituting eq. (8) into eq. (6) yields:

$$\frac{d[M_1]}{d[M_2]} = \frac{k_{1app}[M_1]_0}{k_{2app}[M_2]_0} \exp[(k_{2app} - k_{1app})t] \quad (9)$$

Therefore,

$$G = \frac{[M_1]_0}{[M_2]_0} \exp[(k_{2app} - k_{1app})t] - \frac{k_{2app}}{k_{1app}} \quad (10)$$

and

$$F = \frac{[M_1]_0 k_{2app}}{[M_2]_0 k_{1app}} \exp[(k_{2app} - k_{1app})t] \quad (11)$$

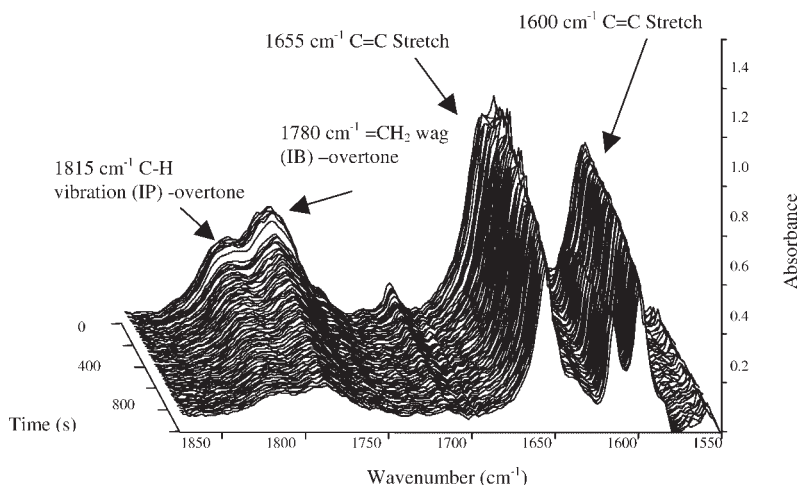


Figure 1.

Real time FTIR monitoring of IB-IP copolymerization. TR probe: $[IB]_0 = 1.45\text{ mol/L}$, $[IP]_0 = 0.55\text{ mol/L}$, $[TMPCl]_0 = 0.035\text{ mol/L}$, $[TiCl_4]_0 = 0.35\text{ mol/L}$, $[DtBP] = 0.007\text{ mol/L}$, MeCl/Hx 40/60 v/v, $T = -80\text{ }^\circ\text{C}$.^[1]

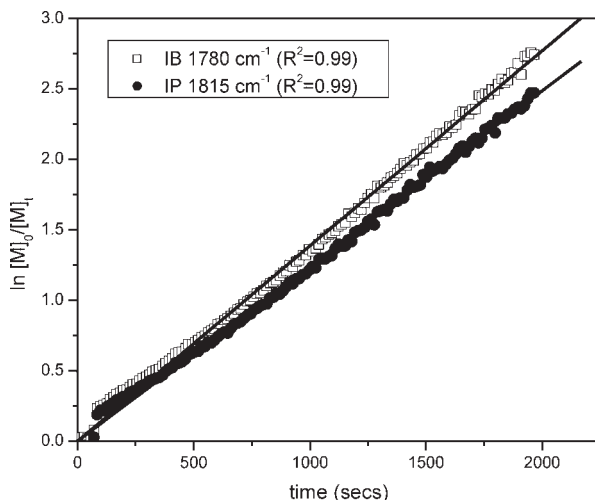


Figure 2.

$\ln ([M]_0/[M])$ vs. time plots for an IB-IP copolymerization monitored by fiber optic *real time* FTIR. Conditions in Figure 1.^[1]

Substituting (10) and (11) into (4) and (5) yields expressions for r_1 and r_2 :

$[M_2]_0$. Therefore this new method is generally applicable for any copolymerization.

$$r_1 = \frac{\frac{[M_1]_0}{[M_2]_0} \exp[(k_{2app} - k_{1app})(t + \delta t)] - \frac{k_{2app}}{k_{1app}} - \left(\frac{[M_1]_0}{[M_2]_0} \exp[(k_{2app} - k_{1app})(t)] - \frac{k_{2app}}{k_{1app}} \right)}{\frac{[M_1]_0 k_{2app}}{[M_2]_0 k_{1app}} \exp[(k_{2app} - k_{1app})(t + \delta t)] - \frac{[M_1]_0 k_{2app}}{[M_2]_0 k_{1app}} \exp[(k_{2app} - k_{1app})(t)]}$$

$$\Rightarrow r_1 = \frac{\frac{[M_1]_0}{[M_2]_0} (\exp[(k_{2app} - k_{1app})(t + \delta t)] - \exp[(k_{2app} - k_{1app})(t)])}{\frac{[M_1]_0 k_{2app}}{[M_2]_0 k_{1app}} (\exp[(k_{2app} - k_{1app})(t + \delta t)] - \exp[(k_{2app} - k_{1app})(t)])}$$

$$\Rightarrow r_1 = \frac{k_{1app}}{k_{2app}} \quad (12)$$

$$r_2 = \frac{k_{1app}}{k_{2app}} \bullet \frac{[M_1]_0 k_{2app}}{[M_2]_0 k_{1app}} \exp[(k_{2app} - k_{1app})t] - \left(\frac{[M_1]_0}{[M_2]_0} \exp[(k_{2app} - k_{1app})t] - \frac{k_{2app}}{k_{1app}} \right)$$

$$\Rightarrow r_2 = \frac{k_{2app}}{k_{1app}} \quad (13)$$

Obtaining Approximate Confidence Intervals for Reactivity Ratio Estimates

The statistical uncertainties associated with estimating r_1 and r_2 using eqs. 12 and 13 arise from uncertainties in the slopes k_{1app} and k_{2app} from the semi-log monomer-consumption plots, which, in turn, are related to the noise in the FTIR data. To demonstrate how this variance propagation from the data to the estimated reactivity ratios occurs, we use a Taylor-series expansion to linearize eq. 17 about the

If k_{app1} and k_{app2} vary significantly with time, this procedure can be applied using short constant-slope parts of the semi-logarithmic plots where $[M_1]/[M_2] \sim [M_1]_0/$

true value \tilde{r}_1 that would be obtained if slopes \hat{k}_{1app} and \hat{k}_{2app} were available from perfect noise-free data:

$$\begin{aligned}\hat{r}_1 = & \tilde{r}_1 + \frac{\partial r_1}{\partial k_{1app}} \Big|_{\tilde{k}} (\hat{k}_{1app} - \tilde{k}_{1app}) \\ & + \frac{\partial r_1}{\partial k_{2app}} \Big|_{\tilde{k}} (\hat{k}_{2app} - \tilde{k}_{2app}) \\ & + \text{higher order terms}\end{aligned}\quad (14)$$

The partial derivatives in eq. 14, which are evaluated at the (hypothetical) perfect noise-free values of the apparent rate constants, are:

$$\frac{\partial r_1}{\partial k_{1app}} \Big|_{\tilde{k}} = \frac{1}{\tilde{k}_{2app}} \quad (15)$$

$$\frac{\partial r_1}{\partial k_{2app}} \Big|_{\tilde{k}} = -\frac{\tilde{k}_{1app}}{\tilde{k}_{2app}^2} \quad (16)$$

Neglecting the higher-order terms in eq. 14, and substituting these partial derivative expressions gives:

$$\begin{aligned}\hat{r}_1 - \tilde{r}_1 = & \frac{1}{\tilde{k}_{2app}} (\hat{k}_{1app} - \tilde{k}_{1app}) \\ & - \frac{\tilde{k}_{1app}}{\tilde{k}_{2app}^2} (\hat{k}_{2app} - \tilde{k}_{2app})\end{aligned}\quad (17)$$

An important statistical theorem for linear combinations of variances^[15] is that, if a random variable, Z , is a linear combination of two other random variables X and Y

$$Z = aX + bY \quad (18)$$

where a and b are constants, and X and Y are independent, then the variance of Z is related to the variances of X and Y by:

$$\sigma_Z^2 = a^2 \sigma_X^2 + b^2 \sigma_Y^2 \quad (19)$$

This theorem is helpful for deriving 95% confidence intervals for the true value of r_1 because, if we assume that the estimates for the slopes \hat{k}_{1app} and \hat{k}_{2app} , which are random variables, are independent because they are obtained from different peaks in the IR spectra, then we can write:

$$\sigma_{r_1}^2 = a^2 \sigma_{k_{1app}}^2 + b^2 \sigma_{k_{2app}}^2 \quad (20)$$

where $a = \frac{1}{\tilde{k}_{2app}}$ and $b = -\frac{\tilde{k}_{1app}}{\tilde{k}_{2app}^2}$ are constants. As a result, we can estimate the

standard deviation of the estimate of r_1 using standard deviations, $s_{k_{1app}}$ and $s_{k_{2app}}$, of the slope parameters \hat{k}_{1app} and \hat{k}_{2app} that are reported by the linear-regression software used for fitting straight lines to semi-log comonomer consumption plots (e.g., see Figure 2), so that:

$$s_{r_1}^2 = a^2 s_{k_{1app}}^2 + b^2 s_{k_{2app}}^2 \quad (21)$$

It is appropriate to use the estimated values \hat{k}_{1app} and \hat{k}_{2app} to compute a and b ^[16] since the true values are unknown. We can then use the resulting estimate of s_{r_1} to calculate appropriate 95 % confidence intervals using the Student t distribution, (if we assume that the random errors in the data are independent and identically Normally distributed). The confidence interval for r_1 is

$$\hat{r}_1 \pm t_{0.025, \nu} s_{r_1} \quad (22)$$

where $t_{0.025, \nu}$ is a value from the Student's t tables, with $\alpha = 0.025$ (i.e., 2.5% of the area to the right) and the confidence interval for r_2 can be obtained by simply switching the values of 1 and 2 in equations (20) to (22). Appropriate values of ν , the approximate number of degrees of freedom, can be calculated using the Fairfield Smith approximation^[17] so that:

$$\nu = \frac{\left((as_{k_{1app}})^2 + (bs_{k_{2app}})^2 \right)^2}{\left(as_{k_{1app}} \right)^4 / (n_1 - 1) + \left(bs_{k_{2app}} \right)^4 / (n_2 - 1)} \quad (23)$$

where n_1 and n_2 are the numbers of data points used to fit \hat{k}_{1app} and \hat{k}_{2app} , respectively. The value of ν obtained from eq. 23 should be rounded down to the next integer value.

If $n_1 = n_2$, or if $n_1 \neq n_2$ but they are both large (>30), as is often the case when FTIR data are used, the Normal distribution can be used instead of the Student t distribution, so that the 95% confidence intervals for r_1 and r_2 can be calculated directly from the half-widths, w_{k1} and w_{k2} of the 95% confidence intervals for k_{1app} and k_{2app} , respectively. Note that by half-widths, we

simply mean that the confidence interval for k_{1app} obtained by linear regression is $\hat{k}_{1app} \pm w_{k1}$. The resulting approximate 95% confidence interval expressions for the true values of r_1 and r_2 are then:

$$\hat{r}_1 \pm \sqrt{\left(\frac{1}{k_{2app}}\right)^2 w_{k1}^2 + \left(-\frac{k_{1app}}{k_{2app}^2}\right)^2 w_{k2}^2} \quad (24)$$

$$\hat{r}_2 \pm \sqrt{\left(-\frac{k_{2app}}{k_{1app}^2}\right)^2 w_{k1}^2 + \left(\frac{1}{k_{1app}}\right)^2 w_{k2}^2} \quad (25)$$

We say “approximate” confidence intervals because equations 12 and 13 are nonlinear functions of the apparent rate constants k_{1app} and k_{2app} . Note that we have assumed that the usual least squares assumptions apply when the slopes k_{1app} and k_{2app} are fitted using the FTIR data (i.e., the model in eq. 5 can represent the data well, and the random errors are independent, identically distributed and Normal). If these assumptions are not valid, (e.g., the residuals from the semi-log plots indicate trends or heteroskedasticity) then it is appropriate to use more sophisticated nonlinear least-squares techniques to obtain the best possible estimates of r_1 and r_2 . In such situations, the values computed from eqs. 12 and 13 will provide useful initial guesses.

Now that we have shown a simple way to estimate r_1 and r_2 from apparent rate constants, an important question arises: how do experimental r_1 and r_2 obtained from apparent rate constants compare with reactivity

ratios $r_1 = k_{11}/k_{12}$ and $r_2 = k_{22}/k_{21}$ obtained from estimates of the true rate constants?

Experimental Measurement of Reactivity Ratios from Pseudokinetic Rate Constants

Table 1 lists data we recently obtained for the copolymerization of IB with styrene (St). In this system, Rapid Monomer Consumption RMC followed by a slower steady rate was observed at certain monomer concentrations and compositions. For these experiments, reactivity ratios values were estimated from both the initial and the steady k_{app} values. These reactivity ratios showed strong dependence on both feed composition and absolute comonomer concentrations. Re-evaluation of earlier data^[18] and our own extended investigations (this will be published elsewhere) clearly demonstrated penultimate effects in IB-St copolymerization, as suggested by the earlier critical analysis of Kennedy et al.^[19]

All of the reactivity ratios reported in Table 1 are statistically significant (i.e., their 95% confidence intervals do not contain zero). It is interesting to note that, at 20 mol% IB in the feed, the relative consumption rates of IB and St are similar in the RMC and the subsequent slower steady rate. This is in agreement with the azeotrope conditions reported by Kennedy and Hull.^[18]

Table 2 lists k_{app} values we reported earlier for IB-IP copolymerizations (IB – M₁ and IP – M₂) for which the terminal model applied,^[1] together with reactivity ratios calculated using eq. (17). These

Table 1.

Instantaneous reactivity ratios in IB-St copolymerizations^[2] $[IB]_0 + [IP]_0 = 0.5$ mol/L.

$[IB]_0$ mol%	Initial Rate				Steady Rate			
	$r_{app}(IB)$	CI	$r_{app}(St)$	CI	$r_{app}(IB)$	CI	$r_{app}(St)$	CI
80	38.43	7.23	–	–	13.53	2.06	0.07	0.01
66	23.92	0.04	–	–	4.34	0.20	0.23	0.01
50	25.92	2.01	–	–	3.44	0.37	0.29	0.02
33	1.24	0.93	0.81	0.78	4.36	0.39	0.23	0.02
20	2.92	0.41	0.34	0.02	2.35	0.15	0.43	0.01

CI = half width of 95% confidence interval.

Table 2.

Reactivity Ratios in IB-IP Copolymerizations obtained using Real-Time FTIR.

[IB] ₀ mol/L	$k_{app}(\text{IB})$ 1/s	$k_{app}(\text{IP})$ 1/s	$r_{app}(\text{IB})$	$r_{app}(\text{IP})$
90.00	0.0040	0.0039	1.05	0.95
79.75	0.0044	0.0042	1.03	0.98
72.50	0.0025	0.0022	1.14	0.88
50.20	0.0015	0.0014	1.07	0.93

values are reasonably close to $r_1 = 1.32$ and $r_2 = 0.74$ predicted from Mayr's LFER and the reported $r_1 = 1.17 \pm 0.01$ and $r_2 = 0.99 \pm 0.02$ (see Fundamentals).

Thus the new method approximates real reactivity ratios in the IB-IP copolymerization for which the M-L equation (1) applies.

Conclusions

Reactivity ratios obtained from apparent monomer consumption rate constants by real-time FTIR monitoring have practical importance since they can be used to predict instantaneous copolymer compositions. However, they have to be treated with caution since they may not represent ratios of true rate constants when the penultimate effect is important, so that they Mayo-Lewis equation does not apply. The new Mayo-Lewis-based method that we propose here for obtaining reactivity ratios from FTIR data provides a simple method for quick computation of reactivity ratios. The method will also be useful for determining initial guesses when more complex nonlinear least squares reactivity ratio estimation methods are used.

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