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Monomer reactivity ratios of styrene–butyl acrylate copolymers at low and high conversions

F. Ziaee and M. Nekoomanesh*
Polymer Research Center of Iran, PO Box 14185/458, Tehran, Iran
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Monomer reactivity ratios in free radical copolymerization of styrene and butyl acrylate monomers at 80°C in toluene solution under reduced pressure were determined for low and high conversions. Mayo–Lewis, Finemann–Ross, inverted Finemann–Ross, Kelen–Tüdős, extended Kelen–Tüdős, Tidwell–Mortimer and Mao–Huglin methods for low conversion and extended Kelen–Tüdős and Mao–Huglin methods for high conversion were used to calculate r_S and r_B in this paper. Using the Mao–Huglin method, for conversions below 15%, monomer reactivity ratio values of 0.887 and 0.216 were calculated for styrene and butyl acrylate, respectively. For conversions greater then 15%, these values were found to be 1.006 and 0.232, respectively. In addition, the reactivity ratios calculated from the second-order Markov reaction were compared with that of calculated using the first-order Markov reaction. © 1997 Elsevier Science Ltd.

(Keywords: styrene; butyl acrylate; monomer reactivity ratio)

INTRODUCTION

Monomer reactivity ratios are important quantitative values to predict the copolymer composition for any starting feed in batch, semi-batch or continuous reactors and to understand the kinetic and mechanistic aspects of copolymerization.

Over the last two decades, a vast amount of data on reactivity ratios has accumulated in the literature for copolymers, especially styrene and butyl acrylate copolymer. The results obtained for the same systems by different methods or by different investigators are usually inconsistent with each other. Monomer reactivity ratios are generally determined at low conversion. In the classic terminal model of copolymerization, it has been suggested that, for a given pair of monomers, the instantaneous copolymer composition is a function of instantaneous feed only[1,2].

The few works on high-conversion copolymerization available in the literature reveal experimental evidence that monomer reactivity ratios are related to conversion under certain conditions[3–5].

The change in the reaction medium with conversion affects the monomer reactivity ratio values. Among several procedures available to determine monomer reactivity ratio, the methods of Mayo–Lewis (ML)[1], Finemann–Ross (FR)[6], inverted Finemann–Ross (IFR), Kelen–Tüdős (KT)[7], extended Kelen–Tüdős (EKT)[8–10], Tidwell–Mortimer (TM)[11], Mao–Huglin (MH)[12], are appropriate for the determination of monomer reactivity ratios at low conversions. Extended Kelen–Tüdős and Mao–Huglin methods consider the drift of comonomer and copolymer composition with conversion. Therefore they are suitable for the manipulation of high conversion data.

In this study, the monomer reactivity ratios of styrene and butyl acrylate for their free radical copolymerization were calculated by various methods and a comparison of these methods was made. The effect of conversion on the monomer reactivity ratio values has also been investigated. In this respect, this is a more detailed study than those available in the literature on the monomer reactivity ratios of styrene and butyl acrylate monomers[13–15].

EXPERIMENTAL

Materials

The monomers, styrene and butyl acrylate (Merck Chemical Co. Inc.), were washed three times with a 5% sodium hydroxide followed by three times with distilled water and then dried over Na_2SO_4. Freshly distilled monomers under vacuum were used each time prior to polymerization. Benzoyl peroxide (Merck) was recrystallized three times from chloroform. Solvents (toluene (Merck) and methanol) were used as received without further purification.

Copolymerization

Copolymerization reactions were conducted in pyrex glass ampoules sealed under vacuum at 10^{-1} mmHg. The ampoules were 14 cm in length with an outer diameter of 8.6 mm.

The monomer, solvent and initiator were weighed and pipetted into numbered ampoules. The ampoules were degassed by several vacuum freeze–thaw cycles, flame-sealed, and subsequently submerged in a 80°C water bath for a recorded time interval. During the reaction, temperature was maintained constant within ±0.1°C of the desired temperature. All runs were carried out by employing 0.05 mol l^{-1} of the initiator and 30% of toluene.

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* To whom correspondence should be addressed

Table 1 Copolymer composition for low conversion

Initial monomer composition of styrene	Copolymer composition of styrene	Conversion (%)
0.1	0.280	4.0
0.2	0.399	4.9
0.3	0.489	4.8
0.3	0.468	10.7
0.4	0.551	5.2
0.5	0.613	5.2
0.5	0.607	13.5
0.6	0.669	11.7
0.7	0.738	9.3
0.8	0.812	8.2
0.9	0.897	6.5

Table 2 Copolymer composition for high conversion

Initial monomer composition of styrene	Copolymer composition of styrene	Conversion (%)
0.1	0.159	56.6
0.2	0.336	45.7
0.3	0.459	28.1
0.4	0.539	30.5
0.5	0.604	35.6
0.5	0.599	50.0
0.6	0.679	31.1
0.7	0.746	28.1

In the early stages of polymerization, the reaction ceased with quenching the ampoules in liquid nitrogen. The reaction mixture was dissolved in toluene and polymer was precipitated out in a 25-fold excess of chilled methanol.

The precipitated polymer dissolved in toluene and precipitated again in methanol at least once more.The filterate was washed several times with fresh methanol. It was then dried at 40°C under vacuum to constant weight.

Copolymer composition analysis

Compositional analysis of the copolymers with respect to the mole fraction of styrene in the copolymer were determined by ^{1}HNMR using a Bruker AC-80 model.

RESULTS AND DISCUSSION

Copolymerization and copolymer composition analysis

The copolymer composition data for low ($<$ 15%) and high ($>$ 15%) conversions are given in *Tables 1* and *2*, respectively.

Monomer reactivity ratios

The Finemann–Ross equation is one of the earliest attempts to linearize the copolymer composition equation:

$$G = r_S H - r_B \qquad (1)$$

where:

$G = X(Y - 1)/Y$;
$H = X^2/Y$;
$X = f_S/f_B$; and
$Y = F_S/F_B$.The inverted FR equation gives r_S as the intercept and r_B as the slope:

$$G/H = -r_B(1/H) + r_S \qquad (2)$$

The FR and inverted FR plots are given in *Figures 1 and 2*.

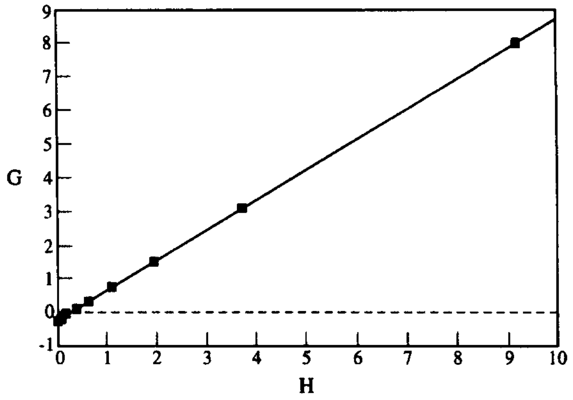

Figure 1 Finemann–Ross plot

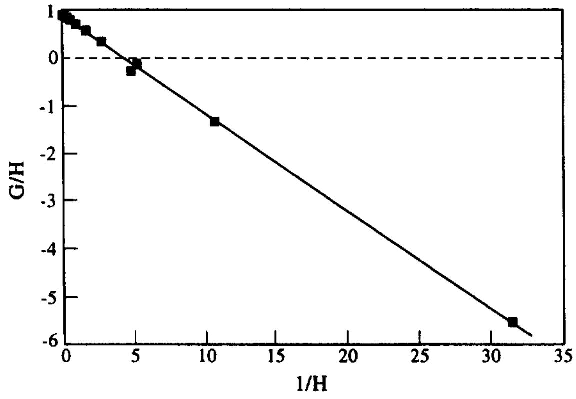

Figure 2 Inverted Finemann–Ross plot

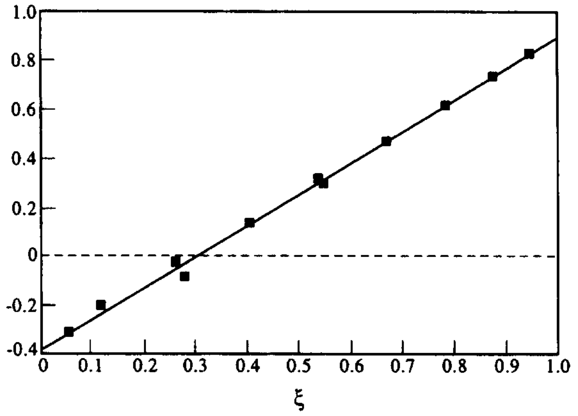

Figure 3 Kelen–Tüdős plot

Kelen and Tüdős (KT) introduced new parameters into the linearized copolymerization equation, such as η, ζ and α:

$$\eta = (r_S + r_B/\alpha)\zeta - r_B/\alpha \qquad (3)$$

where:

$\eta = G/(\alpha + H)$;
$\zeta = H/(\alpha + H)$; and
$\alpha = (H_{max} \cdot H_{min})^{1/2}$.The intercepts at $\zeta = 0$ and $\zeta = 1$ of the η *versus* ζ plot gives $-r_B/\alpha$ and r_S, respectively. H_{max} and H_{min} are the highest and lowest values of H. The KT plot for low conversion data of this system is given in *Figure 3*.

The effect of conversion is considered in the extended Kelen–Tüdős equation. The partial molar conversion of

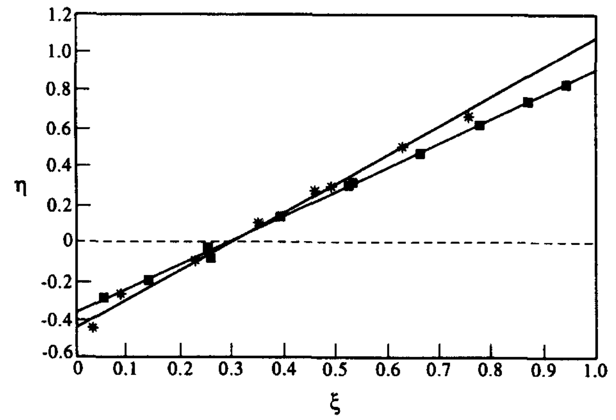

Figure 4 Extended Kelen–Tüdös plot: (■) low conversion; (★) high conversion

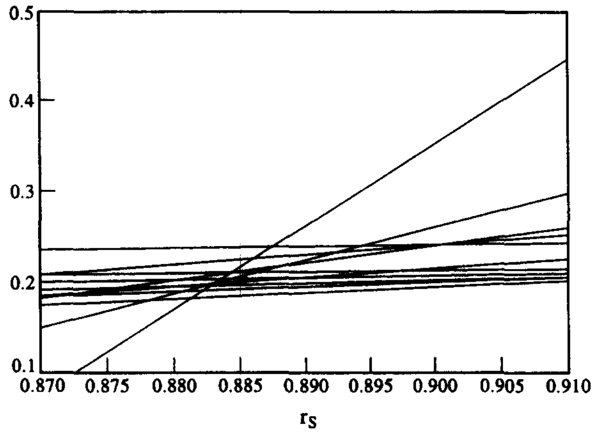

Figure 5 Mayo–Lewis plot

butyl acrylate is defined as:

$$\zeta_B = W(\mu + X)/(\mu + Y) \qquad (4)$$

where W is the weight conversion of polymerization, and μ is the ratio of molecular weight of butyl acrylate to that of styrene. The partial molar conversion of styrene is

$$\zeta_S = \zeta_B(Y/X) \qquad (5)$$

Then:

$$Z = \log(1 - \zeta_S)/\log(1 - \zeta_B) \qquad (6)$$

where:

$H = Y/Z^2$;
$G = (Y - 1)/Z$;
$\mu = G/(\alpha + H)$; and
$\zeta = H/(\alpha + H)$.Extended Kelen–Tüdös plots for low and high conversion samples are given in *Figure 4*.

The other simple procedure for determination of reactivity ratio is the Mayo–Lewis method. In this method using instantaneous copolymer composition, equation reactivity ratios are given by the least summation of the root distance of the point from the lines. The ML plot r_S *versus* r_B is given in *Figure 5*.

The non-linear least-squares procedure as outlined by Tidwell and Mortimer (TM) is considered to be one of the most accurate procedures for determination of monomer reactivity ratio values[16]. The method is a modification of the curve-fitting procedure so that the sum of the squares of the difference between the observed and computed polymer compositions is minimized.

The computation procedure is basically a Gauss–Newton non-linear least-squares method which was modified by Box[17] to assure rapid convergence to a pair of values. A brief description of the method consists initial estimates of r_S and r_B. A set of computations is performed yielding the sum of the squares of the differences between the observed and computed polymer compositions. The sumation is then minimized by iteration, yielding reactivity ratios. This procedure gives unique r_S and r_B values and provides means of evaluating how well the reactivity ratios have been estimated, and if the data are consistent with copolymer composition equation non-linear least-squares procedures such as that of TM are considered to be the only statistically accurate means of determining reactivity ratios from data obtained at low conversions.

The TM procedure consists of the following: given initial estimates of r_S and r_B obtained by some other method, G_i is calculated by

$$G_i = (r_B f_{Bi}^2 + f_{Si} f_{Bi})/(r_B f_{Bi}^2 + 2 f_{Si} f_{Bi} + r_S f_{Si}^2) \qquad (7)$$

The difference d_i, the partial derivates $\partial G_i/\partial r_S$, $\partial G_i/\partial r_B$, and the least-squares estimates b_S and b_B are determined by

$$d_i = F_{Bi} - G_i \qquad (8)$$

$$\partial G_i/\partial r_S = -f_{Si}^2 (r_B f_{Bi}^2 + f_{Si} f_{Bi})/P^2 \qquad (9)$$

$$\partial G_i/\partial r_B = f_{Bi}^2 (r_S f_{Si}^2 + f_{Si} f_{Bi})/P^2 \qquad (10)$$

where

$$P = r_B f_{Bi}^2 + 2 f_{Si} f_{Bi} + r_S f_{Si}^2$$

$$\begin{aligned} b_S = [\textstyle\sum & [(\partial G_i/\partial r_B)^2/(\partial G_i/\partial r_S)^2] \textstyle\sum [d_i/(\partial G_i/\partial r_S)] \\ & - \textstyle\sum [(\partial G_i/\partial r_B)/(\partial G_i/\partial r_S)] \\ & \times \textstyle\sum [d_i(\partial G_i/\partial r_B)/(\partial G_i/\partial r_S)^2]]/C \end{aligned}$$

$$\begin{aligned} b_B = [n & \textstyle\sum [d_i(\partial G_i/\partial r_B)/(\partial G_i/\partial r_S)^2] \\ & - \textstyle\sum [(\partial G_i/\partial r_B)/(\partial G_i/\partial r_S)] \textstyle\sum [d_i/(\partial G_i/\partial r_S)]]/C \end{aligned}$$

$$\begin{aligned} C = n & \textstyle\sum [(\partial G_i/\partial r_B)^2/(\partial G_i/\partial r_S)^2] \\ & - [\textstyle\sum [(\partial G_i/\partial r_B)/(\partial G_i/\partial r_S)]]^2 \end{aligned}$$

Values of $S_k = [\sum (d_i)^2]_k$ for $r_S = r_S^j + [(k - 1)/2] b_S$ and $r_B = r_B^j + [(k - 1)/2] b_B$ are determined for values of $k = 1$, 2 and 3 and $S_4 = [\sum (d_i)^2]_4$ for $r_S = r_S^j + V b_S$ and $r_B = r_B^j + V b_B$, where:

$$V = 0.5 + (S_1 - S_3)/[4(S_1 - 2S_2 + S_3)]$$

S_1 and S_4 (if $S_4 < S_1$) are evaluated by repeating this process with the new estimates of r_S and r_B being r values calculated at S_4. If $S_4 > S_1$, then reevaluate V by first having b_S and b_B. This process is repeated until the sum of the squares of the differences is minimized. For this system with ($r_S = r_B = 10$) initial estimate of reactivity ratios, several iterations are required until the minimum difference obtained. These values are given in *Table 3*.

The Mao–Huglin (MH) method is the newest technique for determination of reactivity ratio at low and high conversions. This is based on a new rearrangement of

Table 3 Results of reactivity ratios using the Tidwell–Mortimer method (initial guess: $r_S = r_B = 10$)

r_S	r_B	$\langle d_i^2 \rangle$
10	10	0.450759502
7.3650050	7.1325600	0.417947995
2.9813150	2.4176960	0.265946179
2.1879650	1.6300400	0.202356461
1.4528350	0.9141369	0.113034364
0.9910042	0.4597653	0.035259023
0.8361094	0.2591624	0.004309260
0.8518048	0.1995471	0.000358880
0.8807692	0.2057518	0.000277504
0.8815998	0.2059323	0.000277429
0.8816164	0.2059359	0.000277428
0.8816760	0.2594890	0.000277428
0.8817015	0.2059544	0.000277428
0.8816966	0.2059534	0.000277428

copolymer composition equation as:

$$\frac{F_S}{F_B} = \frac{r_S (f_S/f_B)^{*2} + (f_S/f_B)^*}{r_B + (f_S/f_B)^*} \tag{11}$$

The quantity $(f_S/f_B)^*$ can be regarded as an average integrated, monomer feed composition. From the preceding discussion, it is clear that $(f_S/f_B)^*$ could completely correct the systematic error produced at any high conversion. If $(f_S/f_B)^*$ is found then the new method is complete without systematic error. Unfortunately, $(f_S/f_B)^*$ could not be measured experimentally.

If it is assumed in the first instance that the true values of r_S and r_B are known, then according to the integrated copolymerization equation it follows that

$$\langle F_S \rangle = \frac{1}{x} \int_0^x F_x(x)\, \mathrm{d}x \tag{12}$$

For the *i*th experimental point, the instantaneous monomer feed composition $(f_S/f_B)_i$,and the instantaneous copolymer composition $(F_S/F_B)_i^c$, at any conversion θ_i can be calculated. The $(F_S/F_B)_i^c$ should be equal to $(F_S/F_B)_i^e$, if the latter experimental quantity can be measured without error.

Although it is not true, at this stage of the argument it is considered deliberately that this calculated $(F_S/F_B)_i^c$ is the same as the instantaneous copolymer composition.

In this situation the corresponding instantaneous monomer feed composition $(f_S/f_B)_i^c$ may be calculated by replacing $(F_S/F_B)_i^c$:

$$(f_S/f_B)_i^c = \frac{\left[(F_S/F_B)_i^c - 1\right] + \sqrt{[1 - (F_S/F_B)_i^c]^2 + 4 r_S r_B (F_S/F_B)_i^c}}{2 r_S} \tag{13}$$

The $(f_S/f_B)_i^c$ calculated in this way will comply with the relationship of differential copolymer composition with both $(F_S/F_B)_i^c$ and the measured $(F_S/F_B)_i^e$, that is:

$$(F_S/F_B)_i^c = \frac{r_S[(f_S/f_B)_i^c]^2 + [(f_S/f_B)_i^c]}{r_B + (f_S/f_B)_i^c} \tag{14}$$

and

$$(F_S/F_B)_i^e = \frac{r_S[(f_S/f_B)_i^c]^2 + [(f_S/f_B)_i^c]}{r_B + (f_S/f_B)_i^c} \tag{15}$$

Table 4 Results of reactivity ratio using the Mao–Huglin method in low conversion (initial guess: $r_S = r_B = 10$)

r_S	r_B	S
0.7366873	0.0061677	2327.829235536
0.8945658	0.2347053	2.060006244
0.8863053	0.2154188	0.009111868
0.8866851	0.2164353	0.002698489
0.8866687	0.2163849	0.002675406

Table 5 Results of reactivity ratio using the Mao–Huglin method in high conversion (initial guess: $r_S = r_B = 10$)

r_S	r_B	S
1.3010623	0.5473968	2.612505024
1.0719738	0.3026209	0.202559805
1.0212563	0.2484097	0.023675018
1.0061861	0.2322683	0.005121412

Then, by using a linear-least squares method such as FR or KT, a plot of the variable combinations of $(f_S/f_B)_i^c$ and $(F_S/F_B)_i^e$ will lead to the same true r_S and r_B. This means that $(f_S/f_B)_i^c$ is exactly equal to $(f_S/f_B)_i^*$ which is being sought.

Of course one cannot know initially the true values of r_S and r_B. If the assumed r_S and r_B are incorrect, the calculated values of $(F_S/F_B)_i^c$ will be different from the measured $(F_S/F_B)_i^e$. The values of $(f_S/f_B)_i^c$ calculated from $(F_S/F_B)_i^c$ via equation (13) can be valid in differential copolymer composition only with $(F_S/F_B)_i^c$, but not with measured $(F_S/F_B)_i^e$. In addition, the values of $(f_S/f_B)_i^c$ calculated from $(F_S/F_B)_i^c$ via the differential copolymer composition equation can be valid.

That is, equation (14) remains valid, but equation (15) does not. Thus the plot of the variable combination of $(f_S/f_B)_i^c$ and $(F_S/F_B)_i^e$ will lead to values of r_S and r_B which are different from the assumed ones. Only after several tests to find the true values of r_S and r_B can the correct $(f_S/f_B)_i^*$ be found and then the newly calculated r_S and r_B will not change. In other words, the criterion that recalculated values of r_S and r_B are equal to those assumed, means that both the true values of reactivity ratios and the correct $(f_S/f_B)^*$ have been obtained.

To demonstrate the accuracy of the MH method, computer simulation of series of data points with low and high conversions are used. The results are given in *Table 4*.

This case is referred to a system for all iteration steps from beginning to end which are shown in *Table 5*. *Table 5* also includes the difference (S), between calculated and measured average copolymer composition.

$$S = \sum [(F_S/F_B)_i^e - (F_S/F_B)_i^c]^2 \tag{16}$$

Monomer reactivity ratios are generally determined at low conversions owing to the ease of the assumption that the drift in the comonomer composition is negligible at low conversions. However, significantly more accurate reactivity ratios can be calculated if the effects of conversion on the comonomer and copolymer compositions are taken into account even at low conversions. The values obtained by the EKT and MH methods are considered in their calculation.

The monomer reactivity ratio of styrene and butyl acrylate obtained by various methods are given in *Table 6*.

Table 6 Results of monomer reactivity ratios calculated using various methods

Low conversion	r_S	r_B
Finemann–Ross	0.884	0.208
Inverted Finemann–Ross	0.865	0.202
Mayo–Lewis	0.883	0.208
Kelen–Tüdős	0.883	0.207
Extended Kelen–Tüdős	0.886	0.196
Mao–Huglin	0.887	0.216
Tidwell–Mortimer	0.882	0.206
High conversion	r_S	r_B
Extended Kelen–Tüdős	1.058	0.239
Mao–Huglin	1.006	0.232

Table 7 Comparison of the results obtained from this work and from Dubé *et al.*[19]

Results in this work at 80°C	
First-order Markov	
$r_S = 0.883$	$r_B = 0.207$
Second-order Markov	
$r_S = 0.892$	$r_S' = 0.856$
$r_B = 0.208$	$r_B' = 0.201$
Results from Dubé *et al.* at 50°C	
First-order Markov	
$r_S = 0.956$	$r_B = 0.183$
Second-order Markov	
$r_S = 0.551$	$r_S' = 0.937$
$r_B = 0.225$	$r_B' = 0.130$

Effect of conversion on the reactivity ratio

As the *Table 6* shows, the monomer reactivity ratio enhances with increasing conversion considering the results obtained by using the EKT or MH methods. There is an increase in r_S value from 0.887 to 1.006 and in r_B from 0.216 to 0.232. Basically in copolymerization systems the reactivity ratios varies with increasing the percentage of conversion[3,18]. The reasons can be explained as follows.

Increasing the percentage of reaction causes an enhancment of viscosity of the reaction media, while the latter changes the monomer diffusion to macroradicals. In other words, at high conversions both the propagation constant and the monomer collision to macroradicals are lowered. At this conversion (at this situation) the effect of penultimate bulky group is considerable and the system tend to adopt second-order Markov statistics, thus affecting the reactivity ratios.

Reactivity ratios in the second-order Markov or penultimate model

The modified copolymer composition equation for the second-order Markov or penultimate model is shown in equation (17)[19].

$$\frac{F_S}{F_B} = \frac{1 + (r'_S\psi(r_S\psi + 1)/(r'_S\psi + 1))}{1 + (r'_B(r_B + \psi)/\psi(r'_B + \psi))} \qquad (17)$$

where

$\psi = f_S/f_B$;
$r_S = k_{SSB}/k_{SSS}$;
$r'_S = k_{BSS}/k_{BSB}$;
$r_B = k_{BBB}/k_{BBS}$; and
$r'_B = k_{SBB}/k_{SBS}$.

Using experimental copolymer composition data from *Table 1* and with the aid of a computer it is possible to estimate r_S, r'_S, r_B and r'_B as adjustable parameters.

The above parameters have been calculated for the present study and the results are shown in *Table 7*. The table also shows the ratios obtaind by Dubé *et al.*[19] for comparison. Copolymerization temperature for present work is higher than that of Dubé *et al.* At higher temperatures the rate of monomer collision to macroradicals increases, thus reducing the effect of penultimate bulky groups on the kinetic constants of propagation, and the whole system approches to ideal situation.

For the ideal situation the result of multiplication of the reactivity ratios are unity. As *Table 7* indicates, for Dubé *et al.* $r_S{\cdot}r_B = 0.174$, while for the present work at low conversion $r_S{\cdot}r_B = 0.184$. The latter is closer to 1, and hence more similar to the ideal system.

CONCLUSIONS

It is possible to calculate the reactivity ratio for the styrene–butyl acrylate copolymer using different methods. Out of the possible techniques, EKT, MH and TM have a better to the experimental results. However, the reactivity ratios are similar (almost independent to the method of calculation) due to the accuracy of measurment.

A trace increase in the reactivity ratios of copolymerization of styrene–butyl acrylate in toluene was observed, indicating that toluene does not reduce the diffusion reduction in chain growth. In addition, it is shown that the system tends to adopt a first-order Markov reaction with increasing temperature.

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