Emulsion Copolymerization of Butyl Acrylate and Glycidyl Methacrylate: Determination of Monomer Reactivity Ratios

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A B S T R A C T

Copolymers of butyl acrylate (BA) and glycidyl methacrylate (GMA) were prepared by batch emulsion copolymerization at 75°C, using potassium persulphate (KPS) as an initiator, sodium dodecylbenzene sulphonate (SDBS) as an emulsifier and sodium bicarbonate as a buffer. Composition of copolymers was determined by elemental analysis and the monomer reactivity ratios were estimated by five conventional linear methods at low monomer conversions, i.e., methods of Mayo-Lewis (ML), Fineman-Ross (FR), inverted Fineman-Ross (IFR), Ezrielev-Brokhina-Roskin (EBR) and Kelen-Tudos (KT). All methods resulted in higher reactivity ratios for GMA comparing to those of BA (ML: \( r_B = 0.15 \) and \( r_G = 1.51 \), FR: \( r_B = 0.22 \) and \( r_G = 1.85 \), IFR: \( r_B = 0.16 \) and \( r_G = 1.57 \), EBR: \( r_B = 0.18 \) and \( r_G = 1.77 \), and KT: \( r_B = 0.30 \) and \( r_G = 1.57 \)). The results also showed that, compared to homogeneous polymerizations (bulk and solution), reactivity ratio of GMA is reduced in emulsion polymerization due to its relative water-solubility, whereas the reactivity ratio of BA is distinctly increased. The effect of the reactivity ratios on the monomer conversion was primarily studied, as well. The results showed that monomer conversion is increased when using higher GMA feed content due to higher reactivity of GMA.

INTRODUCTION

In the study of copolymerization kinetics, determination of monomer reactivity ratios is a challenging area for both the academy and industry. It is important, especially in copolymers with desired physical and chemical properties and in evaluation of their specific final applications [1]. Monomer reactivity ratios allow prediction of a copolymer composition with any starting feed. They are also useful for understanding the kinetics and mechanistic aspects of copolymerization [2]. This can be understood by the number of papers and various citations that provide reactivity ratios for different copolymerization systems.

Among several procedures available to determine monomer reactivity ratio, the methods of Mayo-Lewis (ML) [3], Fineman-Ross (FR) [4], inverted Fineman-Ross (IFR) [4], Ezrielev-Brokhina-Roskin (EBR) [5] and Kelen-Tudos (KT) [6] are appropriate for the determination of monomer reactivity ratios at low conversions.

Emulsion polymerization is an

Key Words:
emulsion copolymerization; monomer reactivity ratios; butyl acrylate; glycidyl methacrylate.
important industrial process in manufacturing of polymer products because of producing high molecular weight polymers and replacement of organic solvents by water, for environmental safety [7]. Acrylic emulsions that are frequently used for surface coating formulations are conventionally based on methyl methacrylate (MMA) and butyl acrylate (BA) which are rather water-insoluble. Recently, some works have focused on emulsions involving functional monomers of glycidyl methacrylate (GMA) having relative water solubility [8-11].

Several researchers have reported the determination of monomer reactivity ratios in emulsion polymerization [12-15]. While Goldwasser et al. [16] reported equal values for monomer reactivity ratios obtained from homogeneous polymerization, other workers such as Bhawal et al. [13], Schuller [17], Guillot [18,19], and Gardon [20] stated that different monomer reactivity ratios had to be defined for emulsion polymerization particularly when comonomers have different solubilities.

Monomer reactivity ratios of BA and GMA have been determined previously for homogeneous systems, e.g., bulk polymerization (\( r_B = 0.12 \pm 0.03 \) and \( r_G = 2.15 \pm 0.14 \)) by Dhal et al. [21] and solution polymerization (\( r_B = 0.16 \pm 0.07 \) and \( r_G = 2.78 \pm 0.32 \)) by de la Fuente et al. [22].

This is the first study dealing with determination of monomer reactivity ratios of BA and GMA copolymerized in emulsion system. Various linear methods were employed and the results were compared with those obtained from homogeneous polymerizations.

### Experimental

#### Materials

Butyl acrylate (BA, Fluka) and glycidyl methacrylate (GMA, Merck) as monomers were purified by vacuum distillation and kept at -4°C prior to polymerization reactions. Potassium persulphate (KPS, Merck), sodium dodecylbenzene sulphonate (SDBS, reagent grade, Merck) sodium bicarbonate and hydroquinone were used without further purification. Distilled water (DW) was employed as the continuous phase. Acetone and methanol (all from Merck) were used for purification of the polymers obtained.

<table>
<thead>
<tr>
<th>Component</th>
<th>Concentration (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>150</td>
</tr>
<tr>
<td>BA</td>
<td>(48 \times X_{BA})</td>
</tr>
<tr>
<td>GMA</td>
<td>(48 \times (1-X_{BA}))</td>
</tr>
<tr>
<td>SDBS</td>
<td>1.440</td>
</tr>
<tr>
<td>NaHCO_3</td>
<td>1.200</td>
</tr>
<tr>
<td>KPS</td>
<td>0.300</td>
</tr>
</tbody>
</table>

\( X_{BA} \) is butyl acrylate weight fraction of samples: S1=0.1, S2=0.2, S3=0.3, S4=0.4, S5=0.6, and S6=0.8.

#### Polymerization

Batch emulsion polymerization was carried out at 75±1°C in a 500-mL 4-necked laboratory glass reactor fitted with a reflux condenser, 3-bladed stainless steel impeller, inlet tubes for nitrogen purge and initiator and inhibitor injections. The components of reaction are given in Table 1. Monomers, water, SDBS as emulsifier and sodium bicarbonate as buffer were introduced into the reactor. The reactor content temperature was brought to 75°C and purged with nitrogen for 30 min to remove any dissolved oxygen prior to the start of reaction. The desired amount of KPS as initiator was dissolved in 2.5 mL distilled water and added to the reactor. To keep monomer conversion below 12%, the polymerization was inhibited by adding hydroquinone (10% aqueous solution, 10 mL) after 30-60 s.

The latex product was dried at room temperature and then adequate methanol was added into it to remove residual monomer, initiator, emulsifier and inhibitor. The remaining polymer was swelled in acetone for 24 h and then maintained in methanol for 24 h to extract the remaining impurities. This procedure was repeated twice, and finally the polymer was kept in methanol for 72 h. Then the samples were dried in a vacuum oven at room temperature to a constant weight.

#### Characterization

Monomer conversion (\( \chi \)) was defined as the ratio of the weight of polymer formed to the weight of initial monomers. After inhibitor addition, some samples (~1 mL) were directly taken from the reactor and dried in a vacuum oven to estimate the stage of
conversion. Elemental analysis was performed with a CHN elemental analyzer (Perkin Elmer Instruments, model Series II 2400, USA).

RESULTS AND DISCUSSION

Copolymer Composition
Elemental analysis as a useful method for quantitative analysis has been employed previously [23-26] to determine the copolymer composition and to estimate the reactivity ratios of monomer. In our recent work, we have determined copolymer composition of poly(BA-co-GMA) by four methods (i.e., $^1$H NMR, FTIR, elemental analysis and titration) [27]. We have found out that some GMA epoxy groups hydrolyze during polymerization. Therefore, the GMA mole percentage values determined by $^1$H NMR, FTIR, and titration methods were expected to be lower than the real value while, being higher by elemental analysis determination. On the other hand, partially cross-linking of polymers results in partial solubility of samples in chloroform, and thus, $^1$H NMR data may be related to a part of the sol fraction of the samples [27]. Finally, elemental analysis was recognized as a preferred method with respect to other methods.

Percentages of carbon (C%), hydrogen (H%) and oxygen (O%) in copolymer samples were determined by CHN elemental analysis. Mole percentages of GMA were calculated on the basis of elemental analysis data and eqn (1) [27] as follows:

$$GMA \text{ (mol\%)} = \left(\frac{6}{7} \frac{C\%}{M_C} - \frac{2}{7} \frac{H\%}{M_H}\right) \sqrt{\frac{C\%}{7 M_C}}$$ (1)

where, $M_C$ and $M_H$ are molar masses of carbon and hydrogen and C% and H% are weight percentages of carbon and hydrogen found by elemental analysis. The results are given in Table 2.

Monomer Reactivity Ratios
From the monomer feed ratios and the copolymer compositions, the monomer reactivity ratios of GMA and BA were determined by five conventional linear methods based on eqn (2) (ML method [3]), eqns (3) and (4) (FR and IFR methods [4]), eqn (5) (EBR method [5]) and eqn (6) (KT method [6]):

$$r_B = f \times \left(\frac{r_G f + 1}{F} - 1\right)$$ (2)

$$G = r_G H - r_B$$ (3)

$$\frac{G}{H} = -r_B \left(\frac{1}{H}\right) + r_G$$ (4)

$$\sqrt{\frac{f k}{k_f}} - \frac{1}{\sqrt{f k}} = r_G \sqrt{k} - r_B \sqrt{\frac{k}{f}}$$ (5)

$$\eta = \left(r_G + \frac{r_B}{\alpha}\right) \zeta - \frac{r_B}{\alpha}$$ (6)

where, $f$, $F$, $r_B$, and $r_G$ are the molar ratios of the monomers in the feed and in the copolymer and reactivity ratios of BA and GMA monomers, respectively. The $G$, $H$, $k$, $\eta$ and $\zeta$ as defined in Table 3 stand for mathematical functions of $f$ and $F$. The parameter $\alpha$ is an arbitrary denominator which produces more homogeneous distribution of data along the $\eta-\zeta$ axes (Figure 1d).

Mayo-Lewis method is a simple procedure to determine the reactivity ratios. In this method for each experiment with different feed and copolymer compositions, $r_B$ values are plotted as a function of various assumed values of $r_G$ according to eqn (2). Each experiment yielded a straight line and the intersection of the lines gives the best values of $r_B$ and $r_G$. The ML plot ($r_B$ versus $r_G$) is given in Figure 1a.

In Fineman-Ross method, $G$ values are plotted...
against H values to yield a straight line with \( r_G \) as its slope and \( -r_B \) as its intercept (eqn 3). The inverted Fineman-Ross plot (\( G/H \) versus \( 1/H \)) gives \( -r_B \) as the slope and \( r_G \) as the intercept (eqn (4)). The FR and IFR plots are given in Figures 1b and 1c, respectively.

The main criticism that can be put forward against the above given methods is that \( r_G \) and \( r_B \) do not play equal roles in the equation of the copolymer composition. The Ezrielev-Brokhina-Roskin method enhances some improvements in this regard, by entering \( k = F/f \) in eqn (3) and dividing it by \( \sqrt{Kf} \) to result in eqn (5) in which \( r_G \) and \( r_B \) play equal roles.

Solving the eqn (5) for all the tests it would result in determining \( r_G \) and \( r_B \). The Kelen-Tudos method (eqn (6)) also intends to prevent the non-symmetrical character of the equation of copolymer composition by introducing new parameters such as \( \eta \), \( \xi \), and \( \alpha \). Plotting the values of \( \eta \) versus \( \xi \) provided a straight line that yielded \( -r_B/\alpha \)

Table 3. Parameters of equations (2)-(6) for copolymerization of BA/GMA.

<table>
<thead>
<tr>
<th>Sample code</th>
<th>( f^a )</th>
<th>( F^b )</th>
<th>( G^c )</th>
<th>( H^d )</th>
<th>( G/H )</th>
<th>( 1/H )</th>
<th>( k^e )</th>
<th>( \eta^f )</th>
<th>( \xi^g )</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1</td>
<td>0.100</td>
<td>0.442</td>
<td>-0.127</td>
<td>0.023</td>
<td>-5.572</td>
<td>43.978</td>
<td>4.407</td>
<td>-1.686</td>
<td>0.101</td>
</tr>
<tr>
<td>S2</td>
<td>0.226</td>
<td>0.771</td>
<td>-0.067</td>
<td>0.066</td>
<td>-1.015</td>
<td>15.170</td>
<td>3.420</td>
<td>-0.496</td>
<td>0.246</td>
</tr>
<tr>
<td>S3</td>
<td>0.387</td>
<td>1.047</td>
<td>0.017</td>
<td>0.143</td>
<td>0.121</td>
<td>7.059</td>
<td>2.708</td>
<td>0.079</td>
<td>0.414</td>
</tr>
<tr>
<td>S4</td>
<td>0.601</td>
<td>1.493</td>
<td>0.199</td>
<td>0.242</td>
<td>0.820</td>
<td>4.130</td>
<td>2.483</td>
<td>0.496</td>
<td>0.545</td>
</tr>
<tr>
<td>S5</td>
<td>1.353</td>
<td>2.919</td>
<td>0.889</td>
<td>0.627</td>
<td>1.418</td>
<td>1.595</td>
<td>2.157</td>
<td>0.815</td>
<td>0.756</td>
</tr>
<tr>
<td>S6</td>
<td>3.608</td>
<td>7.262</td>
<td>3.111</td>
<td>1.792</td>
<td>1.736</td>
<td>0.558</td>
<td>2.013</td>
<td>0.939</td>
<td>0.699</td>
</tr>
</tbody>
</table>

(a) \( f = f_G/f_B \); (b) \( F = F_G/F_B \); (c) \( G = (1-F)/F \); (d) \( H = F/F_e \); (e) \( k = F/F_e \); (f) \( \eta = G(\alpha+G) \); (g) \( \xi = H(\alpha+H) \); \( \alpha = (H_{max}/H_{min})^{1/2} \). \( f_G \): molar fraction of GMA in the feed, \( f_B \): molar fraction of BA in the feed, \( F_G \): molar fraction of GMA in the copolymer, and \( F_B \): molar fraction of BA in the copolymer.

Figure 1. Plots of (a) Mayo-Lewis, (b) Fineman-Ross, (c) Inverted Fineman-Ross, and (d) Kelen-Tudos methods.
and \( r_G \) as intercepts on extrapolation to \( \xi = 0 \) and \( \xi = 1 \), respectively (Figure 1d).

The parameters of eqns (2)-(6) for the monomer-monomer pair of BA/GMA are given in Table 3 and the copolymerization reactivity ratios of BA and GMA are listed in Table 4. The regression coefficient \( (R^2) \) is a statistical measure of how well a regression line approximates the real data points. It can be calculated for each method, by using eqn (7) [28,29].

\[
R^2 = \frac{\sum (F_{exp} - \overline{F})^2}{\sum (F_{model} - \overline{F})^2},
\]

(7)

where, \( F_{exp} \) is the experimentally obtained monomer molar ratio of the copolymer, \( \overline{F} \) is monomer molar ratio in the copolymer obtained by curve fitting of \( F_{exp} \) versus \( f \) values, and \( F_{model} \) is monomer molar ratio in the copolymer obtained by eqn (8) and reactivity ratios achieved by each method. A value of 1.0 for \( R^2 \) indicates that the regression line perfectly fits the data [28,29]. According to the regression coefficient values (Table 4), EBR and FR methods seem to be more reasonable in this study (with \( R^2 \) values are very close to 1.0) compared to other methods specially ML and KT.

The reactivity ratio of BA is less than 1 and that of GMA is greater than 1. The reactivity of growing radicals with BA units, as measured by \( 1/r \), seems to be higher towards GMA monomers relative to its own monomer. The \( r_B \) and \( r_G \) values strongly suggest that the copolymer contains more GMA than in the feed. It is also mentioned in Table 4 that \( r_B \times r_G < 1 \), meaning that the copolymerization is inclined to form random copolymers.

As expected, GMA has higher reactivity ratio than BA. This is due to higher reactivity of methacrylate towards acrylate monomers as a result of steric factors, polarities of monomers and resonance stabilization of their radicals [21,26]. Alternatively, flexibility and free movement of the butyl side group in BA hinders the approach of incoming monomer to react with the radical (shielding effect) [21].

Comparison of the reactivity ratios of GMA and BA obtained from emulsion polymerization with those achieved from homogeneous polymerizations \( (r_B = 0.12 \) and \( r_G = 2.15 \) in bulk [21], and \( r_B = 0.16 \) and \( r_G = 2.78 \) in solution [22]) showed that GMA reactivity is reduced sharply in emulsion polymerization, while the reactivity of BA is increased. These changes due to monomer reactivity ratios can be explained according to the following explanations.

Based on the works of Guillot [17,19] and Schuller [16] it was clear that for the same monomers and by conventional techniques, the reactivity ratios obtained for batch emulsion copolymerization are often different from those obtained for homogeneous (bulk or solution) copolymerizations.

Guillot [19] observed that copolymer composition in emulsion copolymerization of styrene-acrylonitrile (St-AN) could change with variation of partition coefficient of comonomers between two phases (polymer particles and water) and monomer-to-water ratio initially charged into a batch reactor. He found out that increasing the emulsifier concentration increases the water solubility of AN (its comonomer has more solubility in water) and decreases its partition coefficient. Therefore, AN/St molar ratio in the poly-

| Table 4. Copolymerization parameters for emulsion copolymerization of BA/GMA. |
|------------------------|------------------|------------------|------------------|------------------|
| Polymerization Method | \( r_B \) | \( r_G \) | \( r_B \times r_G \) | \( 1/r_B \) | \( 1/r_G \) | \( R^2 \) |
| Emulsion | ML | 0.15 | 1.51 | 0.2265 | 6.67 | 0.66 | 0.7755 |
| | FR | 0.22 | 1.85 | 0.4063 | 4.55 | 0.54 | 1.1453 |
| | IFR | 0.16 | 1.57 | 0.2568 | 6.25 | 0.64 | 0.8751 |
| | EBR | 0.18 | 1.77 | 0.3188 | 5.56 | 0.56 | 1.0676 |
| | KT | 0.30 | 1.57 | 0.4722 | 3.33 | 0.67 | 0.8447 |
| Bulk [21] | EBR | 0.12 | 2.15 | 0.2580 | 8.33 | 0.47 | - |
| Solution [22] | KT | 0.16 | 2.78 | 0.4448 | 6.25 | 0.36 | - |

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mer particles (which is the main loci of emulsion polymerization) and consequently in the final copolymer is being reduced. AN/St molar ratio was also increased by raising the monomer-to-water ratio.

Schuller [16] reasoned that during an emulsion copolymerization the reactivity ratios do not vary. Since conventional analysis is using copolymerization equation (eqn (8)) to determine the reactivity ratios and when one or few of the monomers are relatively water-soluble, eqn (8) will give incorrect results.

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

where, \([M_1]\) and \([M_2]\) are concentrations of comonomers, and \(r_1\) and \(r_2\) are reactivity ratios of comonomers.

Schuller modified the copolymerization equation by considering monomer concentrations at the particle reaction sites and introducing monomer partition coefficients and the monomer-to-water ratio to the equation as follows:

\[
\frac{d[M_{1T}]}{d[M_{2T}]} = \frac{1 + r'_1 \left( M_{1T} / M_{2T} \right)}{1 + r'_2 \left( M_{2T} / M_{1T} \right)} 
\]

\[
r'_1 = r_1 \frac{1 + K_2 \phi}{1 + K_1 \phi} 
\]

\[
r'_2 = r_2 \frac{1 + K_1 \phi}{1 + K_2 \phi} 
\]

where \(M_{1T}\) and \(M_{2T}\) are the total amounts of comonomers initially added to the emulsion reactor, and \(r'_1\) and \(r'_2\) are the modified reactivity ratios of emulsion polymerization. The \(r_1\) and \(r_2\) are the reactivity ratios of homogeneous polymerizations and \(\phi\) is defined as volume ratio of monomer to water. \(K_1\) and \(K_2\) are partition coefficients for each comonomer in the polymer particles and aqueous phase which are given by the following equation:

\[
K_i = \frac{[i]_p}{[i]_w} 
\]

where \([i]_p\) and \([i]_w\) are the concentrations of \(i\)th monomer in the polymer particles and aqueous phases, respectively.

Higher water solubility of GMA comparing to BA (50 versus 2 g/L water at 25°C [30]) resulted in lower partition coefficient \((K_G < K_B)\). Therefore, according to eqn (10), GMA reactivity is decreased in emulsion polymerization relative to its value determined in bulk or solution polymerization \((r'_G < r_G)\). According to eqn (11) BA reactivity is increased \((r'_B > r_B)\) due to a similar reason.

Molar fraction of GMA in the copolymer \((F_G)\) as a function of GMA molar fraction in the feed \((f_G)\) is given in Figure 2. Data are calculated based on our reactivity ratios from emulsion polymerization \((r_B = 0.18\) and \(r_G = 1.77\)) and those for bulk polymerization \((r_B = 0.12\) and \(r_G = 2.15\)) reported by Dhal et al. [21]. Figure 2 presents not only the relationship between molar fraction of monomer in the feed and copolymer but also shows the changing molar fraction of comonomers in the copolymer during polymerization.

According to Figure 2, the GMA molar fraction in the feed is decreased through polymerization period (increasing conversion) because of higher consumption rate of GMA. Molar fraction of GMA in the copolymer will also decrease by increasing conversion due to its decreasing content in the feed.

**Figure 2.** Plots of \(F_G\) vs. \(f_G\) for copolymerization of GMA and BA. Blank squares (□) are data from elemental analysis, solid line (—) is based on EBR method for emulsion copolymerization \((r_B = 0.18\) and \(r_G = 1.77\)), and dash line (- -) is based on reference 21 for bulk copolymerization \((r_B = 0.12\) and \(r_G = 2.15\)).

\[
TT \quad dM_r \quad M_2 \quad r_1 \quad r_2 \quad M_{1T} \quad M_{2T} \quad r'_1 \quad r'_2 \quad K_1 \quad K_2 \quad \phi \quad i \quad \mathrm{emulsion} \quad \mathrm{bulk} \quad f_G \quad F_G
\]
bulk and emulsion is also given in Figure 2. The GMA content of copolymer chains in the emulsion polymerization method is less than that of bulk polymerization method. At higher GMA contents in the feed \((f_G > 0.8)\), the rate of GMA consumption in emulsion polymerization is higher than that of the bulk polymerization (due to sharper slope of the solid cure in \(f_G > 0.8\)). This rate is comparable at medium GMA contents \((0.1 < f_G < 0.8)\). However, the rate of GMA consumption in the emulsion polymerization is less than that of the bulk polymerization at feed with low values of GMA contents \((f_G < 0.1)\).

The reactivity ratios, as kinetic parameters, can influence the rate of copolymerization. According to eqn (13) [31] in Scheme I, the reaction rate has to be elevated for the feed compositions with higher GMA content.

where, \(N_P\) and \(\bar{n}\) are respectively the number of polymer particles per volume and number of radicals per particle, \(N_A\) is the Avogadro's number, and \([M_{GP}]\) and \([M_{BP}]\) are concentrations of each comonomer in polymer particles, respectively. The parameter \(k_{GG}, k_{BB}\) and \(k_{GB}\) are propagation rate constants.

As a preliminary investigation, we conducted the reaction for three comonomer compositions \((\text{GMA} = 10, 20, \text{and 30 wt%})\). These experiments were in agreement with above equations and showed clearly that increasing of GMA feed content was accompanied with the polymerization rate improvement (Figure 3). In addition, the monomer conversion at the end of reaction was found to be higher for the formulations with higher GMA content.

CONCLUSION

Emulsion copolymerization of BA and GMA was carried out at 75°C and the copolymer composition was determined by elemental analysis. Monomer reactivity ratios of BA and GMA were estimated, using conventional linear methods at low conversion (ML: \(r_B = 0.15\) and \(r_G = 1.51\), FR: \(r_B = 0.22\) and \(r_G = 1.85\), IFR: \(r_B = 0.16\) and \(r_G = 1.57\), EBR: \(r_B = 0.18\) and \(r_G = 1.77\), and KT: \(r_B = 0.30\) and \(r_G = 1.57\)). Due to higher water solubility and lower partition coefficient between polymer particle and water phases, GMA reactivity ratio was reduced in emulsion copolymerization compared to homogeneous polymerizations, while BA reactivity ratio was increased.

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