Kinetic Investigation and Characterization of Styrene-Butyl Acrylate Solution Copolymerization

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ABSTRACT

An investigation on the kinetics of free radical solution copolymerization of styrene with butyl acrylate using benzoyl peroxide and toluene, was made at 80 °C using fixed initiator and solvent concentrations. Sequence distribution of styrene and butyl acrylate and determination of copolymer composition by \(^1\)H NMR and \(^{13}\)C NMR are reported. By interpretation of the \(^{13}\)C NMR spectra of the homopolymers and copolymers, assignment of the carbonyl and quaternary carbon atom resonances has been made. It has been then possible to make a quantitative estimation of the compositional triad distributions in the copolymers. The results are found to be in relatively good agreement with calculated triad sequences.

Key Words: copolymerization, styrene, butyl acrylate, triad sequences, kinetic investigation

INTRODUCTION

In industrial polymer production systems, there is a need for better understanding of the processes. The styrene-butyl acrylate system is commercially important for paints, adhesives and coatings. The industrial methods for synthesizing the copolymers are emulsion and solution polymerizations.

Extensive results have been published regarding the kinetics of the homopolymerization of styrene [1], but works on the homopolymerization kinetics of butyl acrylate are comparatively little [2]. One of the earliest studies on styrene-butyl acrylate copolymerization was by Bradbury and Melville [3], who along with the copolymerization in benzene and in bulk, studied their homopolymerizations as well. Some works have also been conducted by Gruber and Knell [4], who reported high conversions and calculated the reactivity ratios using the Meyer-Lowry equation.

Emulsion copolymerization of the monomers have been studied kinetically by Guillaume et al. [5], Cruz et al. [6] and Garcia-Rejon et al. [7]. Semi-continuous copolymerization has been studied by Snuparek-Krška [8], Garcia-Rejon et al.[9], while chain transfer to monomer was examined by Devon and Rudin[10].

Perhaps the most relevant papers on this work were those by Kaszas et al. [11, 12] in their first paper, they deduced the reactivity ratios and initiation rate for the system. Later on, they performed low
conversion rate measurements for bulk and solution copolymerizations at 50 °C. Dube et al. [13] investigated kinetics of the system and proposed a mathematical model for the bulk copolymerization.

Llauro-Darricades et al. [14] and Brar et al. [15] studied the styrene-butyl acrylate copolymer microstructure using NMR spectroscopy.

In this paper we have investigated kinetics of styrene-butyl acrylate solution copolymerization in toluene at 80 °C for a wide range of conversions.

EXPERIMENTAL

Materials
The monomers, styrene and butyl acrylate (Merck), were washed three times with 5% NaOH solution followed by three times of distilled water, dried over Na₂SO₄, and freshly distilled prior to polymerization. Benzoyl peroxide (Merck) was recrystallized three times from chloroform. 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 had 14 cm length with an outer diameter of 8.6 mm.

The monomers, solvent and initiator were weighed and pipetted into designated ampoules. The ampoules were degassed by several vacuum freeze-thaw cycles, then flame-sealed and subsequently submerged in a 80 °C water bath for a recorded time interval. The reaction temperature was maintained constant within ±0.1 °C of the desired value.

All runs were carried out by employing 0.05 mol/L of initiator and 30% of toluene. In the early stages of polymerization, the reaction was quenched by placing the ampoules in liquid nitrogen. The reaction mixture was then dissolved in toluene and the copolymer was precipitated out in a 25-fold excess of chilled methanol. The dissolution and precipitation cycle was repeated at least twice. Then the precipitated polymer was filtered and washed several times with methanol. It was then dried at 40 °C under vacuum to constant weight.

Molecular Weight Analysis
Molecular weights were measured at 30 °C with a gel permeation chromatography (Waters Associates,
model 150-C). Four styragel packed columns with different pore sizes ($10^3$-$10^6$ Å) were used. The mobile phase was tetrahydrofuran with flow rate of 1.5 mL/min. The solution concentration was 0.2 wt %. Calibration of the instrument was performed with nine standard samples of monodisperse polystyrene having molecular weights between $3.0 \times 10^3$ and $1.4 \times 10^6$.

**Copolymer Composition Analysis**

The average copolymer composition of the different samples was determined by $^1$H NMR. The copolymer samples were examined as 2 wt % solutions in deuterated chloroform. The spectra were recorded at 34 °C using Bruker AC-80. Figure 1 gives a typical copolymer spectrum. The copolymer composition was calculated from relative intensities of phenyl ($S_1$) and $-$OCH$_2$-($S_2$) proton resonances, according to the following equation:

\[
\text{Molar fraction of styrene} = \frac{S_1 / 5}{S_1 / 5 + S_2 / 2} \quad (1)
\]

For this state, number of scans were 16 to 32 and the time for each scan was 4 s.

The copolymer samples for $^{13}$C spectroscopy were examined as 4 wt % solutions in the deuterated chloroform at 34 °C. Figure 2 shows the $^{13}$C spectrum of copoly(styrene-butyl acrylate). The figure shows that the α and β carbons of the styrene appear at 40-46 ppm while the quaternary carbon of the benzene ring gives at 143.3-146.1 ppm. The carbon in ortho, meta and para positions appear at 128.6, 127.2 and 126.0 ppm, respectively [14].

The α and β carbons of the butyl acrylate appear at 41.3 and 35-38 ppm, and the C-1, C-2, C-3, C-4 at 63.9, 30.5, 18.9, and 13.5 ppm, respectively, and that of carbonyl carbon at 175-177 ppm.

Measurement of copolymer composition is possible using the ratio of the integrals of the carbon peaks via eqn (2). In this equation, $S_5$ is the integral of the benzene ring carbons which appeared at 126-128.6 ppm and $S_1$, $S_2$, $S_3$ and $S_4$ are the integrals of C-1, C-2, C-3, C-4, respectively.

\[
\text{Molar fraction of styrene} = \frac{S_5 / 5}{S_5 / 5 + (S_1 + S_2 + S_3 + S_4) / 4} \quad (2)
\]

It is also possible to calculate molar fractions using $S_1$, $S_2$, $S_3$ and $S_4$ individually but due to noisy

![Figure 2. $^{13}$C NMR Spectrum of styrene-butyl acrylate copolymer after 2500 scans.](image)

The flip angle was 90° and each scan time was 8 s. The number of scans were 2500.
base line which cause an enhancement in error the equation of the integrals, eqn (2), was used.

RESULTS AND DISCUSSION

Copoly(styrene-butyl acrylate) Behaviour

Figure 3 represents the conversion-time curve at different monomer feed compositions. As the figure shows with increasing the butyl acrylate in feed, the copolymerization rate is enhanced.

Figures 4 and 5 show the cumulative copoly-
Figure 7. Conversion versus time for copolymerization.

position curve plotted by given \( r_s \) and \( r_B \) together with NMR experimental results. As the figure shows there is a good agreement between experimental results and calculated values.

**Calculation of Copolymerization Rate**

Copolymerization rates were determined using conversion-time curves at low conversions (Figure 7).

From eqn (3) the parameter \( \left( \frac{fK_p}{K_t} \right) \) was extracted for different mole fractions using pseudokinetic model [19]. Where \( K_p \) and \( K_t \) are kinetic constants for propagation and termination, respectively and \( f \) is initiator efficiency.

The value for \( dx/dt \) was determined from initial slope of conversion-time curve, \( K_d \) [16] was computed from eqn (4) and \( \varepsilon \) [13] is estimated from linear regression of eqn (5) by different mole fractions. The values \( x \) and \( t \) were selected from the last point of low conversion point sets.

\[
\frac{dx}{dt} = K_p \left( \frac{2fK_dT_0}{K_1(1-\varepsilon x)} \right)^{1/2} (1-x) \exp(-1/2K_d t) \tag{3}
\]

\[
K_d = 1.073 \times 10^{14} \exp(-14895/T) \tag{4}
\]

\[
\varepsilon = -0.16958 - 0.00669 f_s \tag{5}
\]

Different values for \( \left( \frac{fK_p}{K_t} \right) \) against \( f_B \) are reported in Table 1. It can be seen that by increasing the mole fraction of butyl acrylate in initial feed the ratio of \( \left( \frac{fK_p}{K_t} \right) \), is increased. Dube et al. [13] performed the same calculation for bulk styrene-butyl acrylate copolymer using AIBN at 50 °C. The results in Figure 3 indicate that gel effect decreases considerably. It seems that presence of 30 mol % of toluene reduces viscosity while at the same time enhances macroradicals diffusion and hence reduces the gel effect.

Molecular weight measurement results (Figure 8) disclose the same conclusions. Gel effect is lowered and polymerization kinetic approaches to classic polymerization kinetic. Obviously GPC calibration curve is for linear polymer and at high conversions chain branching is dominant and consequently molecular weight measurements have some deviations from real values, but toluene has a high transfer constant and its concentration (30%) is high enough to decrease polymer branching considerably. The observation of easy solution of the copolymer in THF at room temperature is a good reason for this conclusion.

**Table 1. \( \left( \frac{fK_p}{K_t} \right)^{1/2} \) versus \( f_B \).**

<table>
<thead>
<tr>
<th>( f_B )</th>
<th>( \left( \frac{fK_p}{K_t} \right)^{1/2} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.2</td>
<td>0.3033</td>
</tr>
<tr>
<td>0.5</td>
<td>0.3419</td>
</tr>
<tr>
<td>0.7</td>
<td>0.3717</td>
</tr>
</tbody>
</table>

**13C NMR Results**

According to Figure 2, there are two key positions for
studying microstructures. First position belongs to quaternary carbon of styrene (143.3–146.1 ppm) and the second is that of the carbonyl group carbon of butyl acrylate monomer (175–177 ppm). It is clear that if the monomer sits next to the same or other monomers there would be some resonance shifts in corresponding spectra [14].

Possible triads with central styrene are BSB, SSB and SSS and those with central butyl acrylate are SBS, BBS and BBB. The area under corresponding curves makes it possible to measure their contents in the copolymer chains.

Figures 9 and 10 show the extended state of quaternary carbon of styrene benzene ring and of butyl acrylate carbonyl group, respectively, and show corresponding monomeric areas.

Using the spectra, it is possible to study triad sequence distribution of styrene and butyl acrylate in copolymer chains.

The following calculations are accomplished according to references 14 and 15. Triad sequence concentrations of styrene and butyl acrylate for the copolymer can be computed, when the normalized areas under the curves for 50/50 monomer composition (Figures 9 and 10) are available.

Using reaction rates in polymerization kinetics in 1st Markov or terminal model [17, 18], it is possible to compute the probability of coupling the same monomer adjacent to each other. For example, probability of SS diad sequence formation in copolymer chain $P_{SS}$ can be calculated by equation (6).

$$P_{SS} = \frac{R_{BS}}{R_{SS} + R_{SB}} = \frac{K_{SS}S'S}{K_{SS}S'S + K_{SB}S'B} = \frac{r_S S}{r_S S + B}$$

where $R_{SS}$ and $R_{SB}$ are addition rate constants of S and B monomers to macroradicals with styrene end ($K_{SS}$ and $K_{SB}$ are corresponding propagation rate constants) and $r_S$ and $r_B$ are reactivity ratios of styrene and butyl acrylate monomers. Similarly, $P_{SB}$, $P_{BS}$, $P_{BB}$ for formation of SB, BS and BB diad sequences, respectively, are computed by following relations.

$$P_{SB} = \frac{B}{r_S S + B}$$

$$P_{BS} = \frac{B}{r_S B + S}$$

$$P_{BB} = \frac{r_B B}{r_B B + S}$$

and finally triad sequence formation probabilities can

![Figure 9. Expanded spectrum of styrene quaternary carbon.](image)

![Figure 10. Expanded spectrum of butyl acrylate carbonyl carbon.](image)
Figure 11. Average triad distribution versus conversion in a styrene center with $f_{SB}=0.5$.

be derived by eqns 10–15.

\[ (SSS) = P_{SS}^2 \]  
\[ (SSB) = P_{SS} \times P_{SB} \]  
\[ (BSB) = P_{SB}^2 \]  
\[ (BBB) = P_{BB}^2 \]  
\[ (BBS) = P_{BB} \times P_{BS} \]  
\[ (SBS) = P_{SB}^2 \]

\[ \bar{n}_S = \frac{(BSB) + (SSS) + (SSB)}{2} \]  
\[ \bar{n}_B = \frac{(BSB) + (SSB) + (BBB)}{2} \]

All mentioned equations are based on instantaneous parameters of system. Whereby, increasing the conversion in a batch reactor, $S/B$ ratio would vary and all equations vary accordingly. So the study of mentioned variations should be based on cumulative properties of the system. In order to do so cumulative properties of the system should be determined by integration of mentioned equations. For example, cumulative property of SSS formation is

<table>
<thead>
<tr>
<th>Conversion (%)</th>
<th>S-Centred triads</th>
<th>B-Centred triads</th>
<th>Length S</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>SSS</td>
<td>SSB</td>
<td>BSB</td>
</tr>
<tr>
<td>20</td>
<td>0.2075</td>
<td>0.2965</td>
<td>0.4959</td>
</tr>
<tr>
<td>59.5</td>
<td>0.18</td>
<td>0.32</td>
<td>0.5</td>
</tr>
<tr>
<td>90.5</td>
<td>0.1779</td>
<td>0.3369</td>
<td>0.4851</td>
</tr>
<tr>
<td></td>
<td>0.20</td>
<td>0.30</td>
<td>0.50</td>
</tr>
<tr>
<td></td>
<td>0.1416</td>
<td>0.4118</td>
<td>0.4465</td>
</tr>
<tr>
<td></td>
<td>0.08</td>
<td>0.48</td>
<td>0.44</td>
</tr>
</tbody>
</table>

Table 2. Sequence distribution values of triads and average length of styrene monomer sequence versus conversion at $f_{SB}=0.5$. 
Kinetic Investigation and Characterization of Styrene-Butyl Acrylate

defind by eqn 18, in which \( x \) is conversion [14].

\[
<SSS> = \frac{\int_0^x SSS(x) \, dx}{x}
\]  (18)

According to eqn (18) and considering the reactivity ratios it is possible to plot the variations of triad sequence distributions of styrene and butyl acrylate against conversion. This plot can be seen in Figures 11 and 12. As the figures show, experimental data and theoretical values of SBS and BSB are greater than other triad sequences while those of SSS and BBB are lower than others. Both experimental and theoretical curves indicate that copolymers are from alternative class. Increasing values of BBB and decreasing values of SSS with conversion are due to higher reactivity ratio coefficient of styrene. This implies that feed mole fraction of styrene would be lowered by increasing conversion.

Table 2 shows number average length of styrene monomer both theoretically and experimentally.

CONCLUSION

In styrene and butyl acrylate copolymerization, by increasing the mole fraction of butyl acrylate in feed, reaction rate increases.

Measurement of copolymer composition is possible with \(^{13}\)C and proton NMR methods but proton NMR is fast and exact.

The abundance of SBS and BSB triads in comparison to other triad sequences specially SSS and BBB is an evidence for coming to conclusion that styrene-butyl acrylate copolymer produced by this condition is more an alternative copolymer.

REFERENCES


