

Observations on styrene-hydroxyethyl acrylate and styrene-hydroxyethyl acrylate-ethyl acrylate polymerizations

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Summary

Several experimental observations are reported on the free radical polymerization of hydroxyethyl acrylate (HEA) in its co- and ter-polymerization with styrene (Sty) and ethyl acrylate (EA) initiated by 2,2'-azobisisobutyronitrile (AIBN) in bulk. Reactivity ratios were estimated for the system Sty/HEA using the error in variables model (EVM). Kinetic studies over the full conversion range investigated the effects of feed composition, initiator concentration and temperature. Limited observations are reported for the Sty/HEA/EA terpolymerization on the effect of varying HEA levels.

Keywords: Hydroxyethyl acrylate; styrene; ethyl acrylate; reactivity ratios; copolymerization kinetics.

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Introduction

In general, there are few reported studies of any polymerization involving HEA. This may be in part due to the difficulties in analysis of its polymers stemming from the fact that its polymerization typically leads to high molecular weight products through crosslinking reactions caused by impurities and/or transfer reactions. These problems have been the subject of a limited number of previous investigations. It has been pointed out that hydroxyalkyl acrylate monomers usually contain significant concentrations of divinyl crosslinking agents which are side products of monomer synthesis [1]. Yocum and Nyquist [2], have presented a detailed mechanism of gelation caused by side products in the monomer. They found that the crosslinking observed in such monomer systems was the result of both polymerization of divinyl impurities, such as ethylene glycol diacrylates, and transfer reactions to polymer.

In another study curing rates for HEA and other similar monomers have been compared [3]. Dilatometry was used to examine kinetics of ultra-violet curing (using the n-butyl ether of benzoin as photoinitiator). It was concluded that the curing rate for HEA was several times faster than 2-ethylhexyl acrylate, 2-hydroxyethyl methacrylate, hydroxypropyl acrylate and hydroxypropyl methacrylate.

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Chow conducted solution copolymerizations of HEA with Sty in benzene at 60°C [4]. Data obtained were used to determine reactivity ratios for the monomers (see Table 1). Monte Carlo simulations have been used to predict molecular weight, molecular weight distribution, and composition of Sty/HEA copolymers produced in the presence of chain transfer agent[5]. Another study has also used Monte Carlo simulations to assess composition, molecular weight distribution, monomer sequence distribution, and chemical heterogeneity in Sty/HEA/butyl acrylate terpolymerization [6].

Table 1 Styrene-2-Hydroxyethyl acrylate (monomer 2) reactivity ratios

| r_1 | r_2 | Reference |
|-------|-------|--------------------------------|
| 0.38 | 0.34 | [4] |
| 0.66 | 0.45 | industrial source ^a |
| 0.360 | 0.311 | [5] |

^a Personal communication, industrial source.

Catala *et al.*[7] studied the copolymerization of HEA with methyl acrylate, EA and butyl acrylate using AIBN as the initiator at 60 °C. The overall conclusion from the study was that an increase in the size of the ester group favours introduction of HEA into the copolymer.

The current study may be broken down into two parts. The major part of the project was devoted to the copolymerization of Sty and HEA. An examination of reactivity ratios was followed by an examination of full conversion range kinetics looking at various experimental variables; namely, feed composition, temperature and initiator concentration. The second part of the study looked at selective full conversion range experiments for the terpolymerization of Sty/HEA/EA to ascertain the effect on reaction rates of varying proportions of HEA in the feed.

Experimental

Polymerization experiments were carried out as described previously [8], except for feeds that were high in HEA. Preliminary work with feeds richer in HEA showed that more rigorous procedures were needed to remove residual HEA from the polymer. When the mole fraction of HEA in the feed was 0.5 or greater, the product polymer would not readily precipitate from ethanol. Therefore, polymer was precipitated using distilled water. After isolation, the polymer was swollen or dissolved (dependent on the level of HEA) in DMSO or acetone and then treated with a 10-fold excess of methanol. The polymer was once more isolated, the overall procedure repeated twice, and the products were subsequently dried.

Results and Discussion

A. Sty/HEA Copolymerization. Reactivity Ratio Experiments

These experiments were planned using the Tidwell and Mortimer (1965) D-optimal design [9] using reactivity ratio values reported previously [5]: r_1 (STY) = 0.36 and r_2 (HEA) = 0.31 (see Table 1). This gave values for the optimal feed compositions (mole fractions) of $f_{\text{Sty},0}^f = 0.8477$ and $f_{\text{Sty},0}^{f'} = 0.1347$. In these experiments, the AIBN concentration used was 0.05 mol/L and the temperature was 50°C.

The initial stage in the design was performed by running several replicate reactions to low conversion at the two monomer feed compositions and then analyzing the resultant polymer for composition by ^1H NMR. The experimental results are presented in Table 2.

Table 2. Sty/HEA copolymerization. Summary of data obtained in different stages of the reactivity ratio estimation

| Stage # | Feed Composition | Copolymer Composition Range (F_{sty}) | No. of Replicate Experiments |
|---------|------------------|--|------------------------------|
| 1 | 0.848 | 0.698-0.721 | 4 |
| | 0.135 | 0.211-0.334 | 4 |
| 2 | 0.885 | 0.792-0.820 | 8 |
| | 0.499 | 0.544-0.587 | 4 |
| 3 | 0.920 | 0.847-0.865 | 3 |
| | 0.750 | 0.696-0.704 | 4 |
| 4 | 0.1493 | 0.310-0.342 | 3 |

Conversion levels were controlled to between 4 and 6.5%, low enough to avoid composition drift. In the compositional analyses, HEA composition was determined from the combined integrals of the O-H and O-CH₂- regions. It was noted that the spread of copolymer compositions obtained for $f_{\text{Sty},0}^{f'} = 0.1347$ ($F_{\text{sty}} = 0.334-0.211$) was higher than expected from NMR analysis of replicate samples (typical error = 5%). This suggested some inconsistencies in the experimental procedures. These data were used in the calculation of reactivity ratios by EVM [10]. The errors incorporated in the EVM analysis were 0.0055% for the feed composition and 5% for the measured copolymer composition [8]. The point estimates obtained for the reactivity ratios were $r_1 = 0.28$ and $r_2 = 0.29$.

Following this set of experiments an attempt was made to validate the new reactivity ratios. Feed levels based on the Tidwell-Mortimer criterion and the new reactivity ratios were assessed and another set of polymerizations carried out. The

resulting feeds were $f'_{\text{Sty},0} = 0.879$ and $f''_{\text{Sty},0} = 0.125$; reaction conditions were as for the first stage. However, problems were encountered with the polymerizations for $f''_{\text{Sty},0} = 0.125$; in four replicate experiments conversion levels ranged from 9 to 18%. This range indicated an obvious problem with the experimental methodology for this system. Reactivity ratio calculations made with this set of experimental data were not regarded as reliable.

These results led to a reassessment of the compositions obtained in the first set of experiments when $f'_{\text{Sty},0} = 0.135$. It was likely that the wide range of compositions obtained could be explained by residual HEA (which is relatively involatile) polymerizing after isolation of the polymer when subjected to the final drying at 70°C. This would skew the copolymer compositional analysis to give proportionally high levels of HEA.

In an attempt to circumvent this problem, a new approach to reactivity ratio estimation was considered. Burke et al. [11] have described an alternate method of design to that of Tidwell and Mortimer. They have shown how reactivity ratios may be accurately estimated when a limiting constraint is placed on one of the feed levels used. It was felt that this type of design may be useful for the Sty/HEA system because it appeared that most difficulties arose when the feed was high in HEA. It was therefore rationalised that if an upper limit was placed on the HEA level in the feed, more reliable analytical results could be collected.

For the initial step in this analysis we chose a minimum level of $f'_{\text{Sty},0} = 0.5$. According to [11] the second feed level was $f'_{\text{Sty},0} = 0.884$. The reaction conditions and initiator concentration were as before. The variation in product work up (detailed in the experimental section) was used to isolate the polymer. The results of these runs in terms of feed and copolymer composition are presented in Table 2 (stage 2). Replicate NMR spectra were run for the products of $f'_{\text{Sty},0} = 0.885$ to check the experimental variability in the technique and the effect of different solvents. The level of HEA in the polymer was based on the integral of the O-CH₂ (4H per mole) signal for samples run in deuteriochloroform, whereas for samples run in D6-DMSO it was based on the integral of the O-H signal (1H per mole). The compositions obtained for samples run in both solvents were in good agreement indicating that the two methods were compatible. An EVM analysis of the results gave point estimates of $r_1 = 0.399$ and $r_2 = 0.070$. However, the 95% joint confidence interval from the calculations (Figure 1, ellipse 2) contained values of r_2 that were less than zero.

In order to obtain further information about the effect of setting constraints on the reactivity ratio determination, a further pair of feed levels was examined. The constraining level was $f'_{\text{Sty},0} = 0.75$ and the second feed was correspondingly $f'_{\text{Sty},0} = 0.92$ (r_1 used was 0.28 from stage 1). Results from these experiments are presented in Table 2 (stage 3). EVM analysis of the results gave point estimates of $r_1 = 0.439$

and $r_2 = 0.108$. Once again, the 95% joint confidence interval from the calculations (Figure 1, ellipse 3) contained values of r_2 that were less than zero.

The indication from the sets of experiments using feed constraints was that r_1 could be assumed to be close to 0.4 but the results could not give accurate estimates for r_2 . The final stage in the reassessment of these reactivity ratios was to run another low Sty feed ($f_{\text{sty},0}^{\prime} = 0.149$) and to isolate the polymer by a more rigorous experimental procedure. The composition results for the polymer isolated by the different procedure were notable in that the spread of values was within the normal error range for NMR analysis (see Table 2, stage 4) and that the level of HEA was lower than for similar experiments carried out in Stage 1.

The final EVM analysis used data from this run plus all the data from stages 2 and 3. This gave a final evaluation of $r_1 = 0.465$ and $r_2 = 0.204$ with a relatively small confidence interval (Figure 1, ellipse 4). The conclusion drawn from the final results is that the data obtained in stage 1 (and those of previous studies) lead to an underestimation of r_1 and to values for r_2 being overestimated.

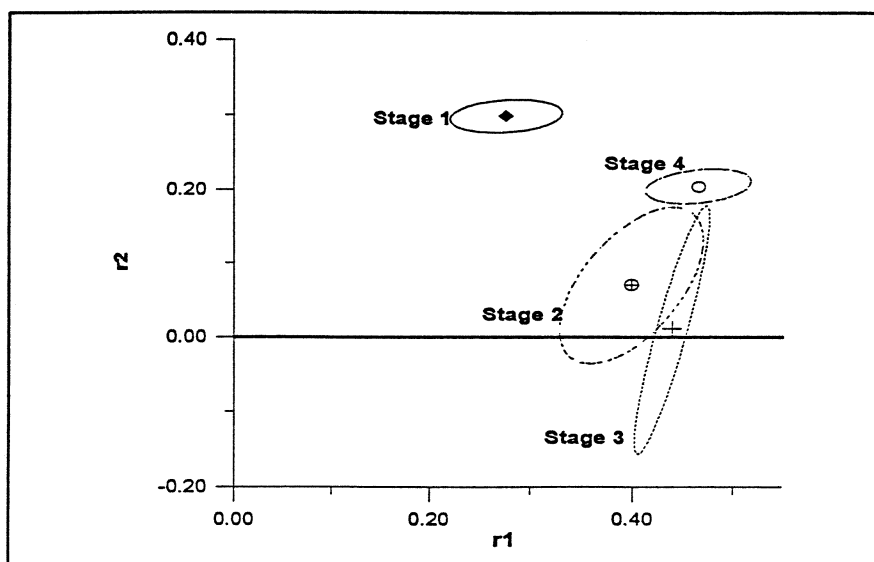


Figure 1. Sty/HEA Copolymerization. Reactivity Ratio Estimates and 95% Posterior Probability Contours from Different Stages of Analysis.

A possible reason that may be considered for variability in reactivity ratio values may be polarity change in the copolymer and monomer mixture, depending on the initial comonomer feed composition. The effect of solvent on the reactivity ratios of styrene and 2-hydroxyethyl methacrylate has been investigated by Lebduska *et al.* [12]. Using N,N-dimethyl formamide, isopropyl alcohol, n-butyl alcohol, and toluene as solvents, they showed that the polarity of the reaction medium strongly affected the

reactivity ratios. If HEA is considered not only as a monomer but also as a solvent for its own copolymer, then it is possible that the polarity changes across the range of feeds may give rise to varying reactivity ratios.

B. Sty/HEA Copolymerization. Full Conversion Range Studies

A 2^3 factorial design was conducted to investigate the effect of temperature, initiator concentration, and initial comonomer feed composition primarily on rates and where possible on composition and MW development. Temperature levels of 40 and 50 °C and initiator concentrations of 0.025 and 0.05 M were chosen as conditions that would allow for isothermal polymerizations. The basic design was to examine two different initial feed composition levels selected to give the maximum composition drift as conversion increases. Additional runs were conducted at the “azeotropic” compositions calculated using reactivity ratios obtained in both stages 1 and 4.

From now on, and due to space limitations, we will only give representative plots of results. No other details are given, unless the obtained trends are unexpected.

Figures 2 to 4 show conversion versus time behaviour, whereas Figure 5 plots copolymer composition versus conversion (consistent with azeotropic behaviour within experimental error).

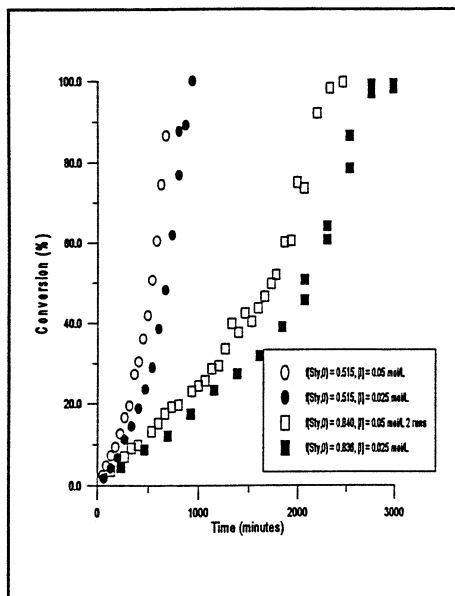


Figure 2. Sty/HEA Copolymerization. Reaction Rates for $T = 40^{\circ}\text{C}$. Effect of Initiator Concentration and Feed Composition.

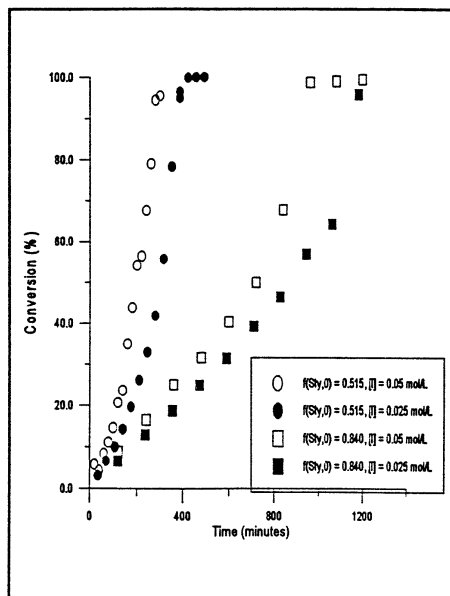


Figure 3. Sty/HEA Copolymerization. Reaction Rates for $T = 50^{\circ}\text{C}$. Effect of Initiator Concentration and Feed Composition.

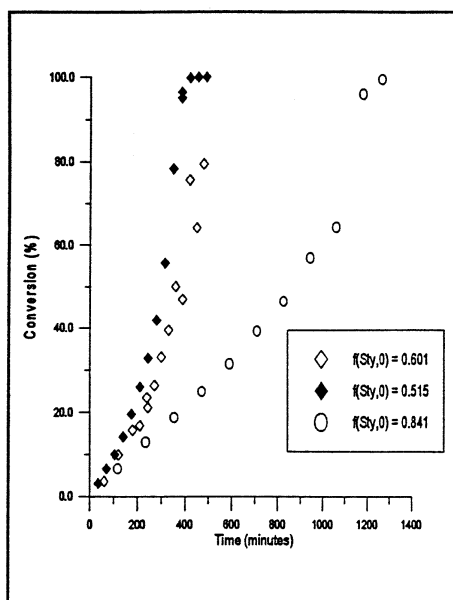


Figure 4. Sty/HEA Copolymerization. Reaction Rates at 50°C, $[I] = 0.025M$. Effect of Feed Composition.

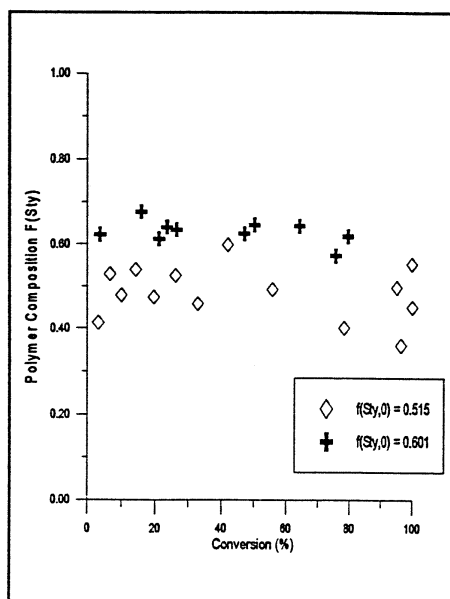


Figure 5. Sty/HEA Copolymerization. Trends in Polymer Composition for Azeotropic Feed Composition.

C. Sty/EA/HEA Terpolymerization

Experiments were limited to the examination of reaction rates at monomer feeds containing relatively low levels of HEA because of difficulties encountered in the copolymerization studies. The results are shown in Figure 6.

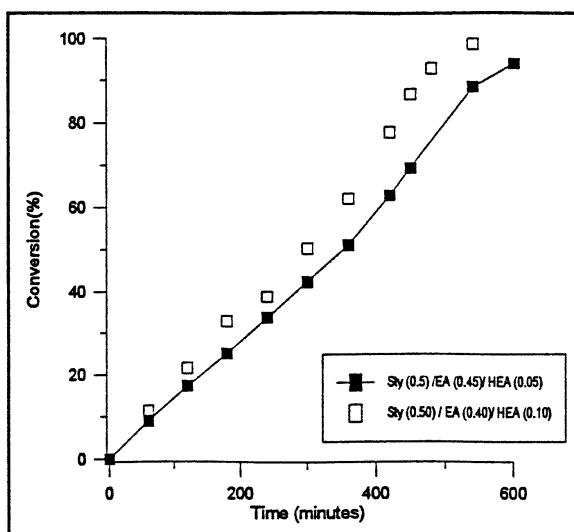


Figure 6. Sty/EA/HEA Terpolymerization. Reaction Rates. Effect of Monomer Feed Ratio. $T = 60^{\circ}C$, $[I] = 0.05 \text{ mol/L}$.

Concluding Remarks

Several insights into multicomponent polymerizations involving HEA have been obtained. The reactivity ratio estimation study for Sty/HEA copolymerization provided a classic example of how misleading results may be obtained if care is not taken in isolation of polymers from residual monomers. The final values obtained for the reactivity ratios are notable in that they differ from those obtained previously.

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