

Determination of Monomer Reactivity Ratios in Styrene/2-Ethylhexylacrylate Copolymer

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ABSTRACT: The monomer reactivity ratios for styrene/2-ethylhexylacrylate in bulk at 80°C were investigated by studying the resulting copolymer composition via ¹H-NMR. Composition results were summarized and various methods were employed to estimate the reactivity ratios including the use of the Error-in-Variables-Model (EVM) approach by using the Mayo–Lewis model. The estimates of the reactivity ratios from the EVM method are found to be $r_s = 0.979$ and

$r_{\text{EHA}} = 0.292$. The resulting copolymer has a tendency toward alternation with an azeotrope of $f(\text{styrene}) = 0.972$. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 92: 3368–3370, 2004

Key words: styrene; 2-ethylhexylacrylate; copolymerization; modeling; radical polymerization

INTRODUCTION

Copolymerization of styrene/2-ethylhexylacrylate (EHA) has attracted attention in recent years because of several applications of the copolymer. Acrylic polymer latices are widely used for adhesives, paints, and varnishes. These applications require the formation of a continuous film, and hence, the glass transition temperature of the polymer, T_g , should be below room temperature. Polymers having a low T_g are used for pressure-sensitive adhesives. Because the polymer becomes softer as the size of the ester group increases, *n*-butyl acrylate and 2-ethylhexylacrylate are basic components of the acrylic latices.^{1,2} The T_g of poly(EHA) is approximately 223 K, while that of polystyrene is 373 K. Varying the concentration of styrene in the copolymer acts as a control for the final T_g .

Because the properties of the copolymer vary with styrene content, it is necessary to determine the copolymer composition before application of the final product.³ At the temperature being considered (80°C), depropagation of either monomer is negligible and the copolymer composition for this system can be calculated by using the Mayo–Lewis equation.⁴ However, to use the model for further calculations of copolymer characteristics, estimates of the reactivity ratios must be obtained. In this work, different techniques (both

linear and nonlinear) are utilized to obtain point estimates of these reactivity ratios including Fineman–Ross (FR) and Inverted Fineman–Ross (IFR),⁵ Yezrielev–Brokhina–Roskin (YBR),⁶ Kelen–Tüdös (KT),⁷ Extended Kelen–Tüdös (EKT),⁸ Mao–Huglin (MH),⁹ Mayo–Lewis (ML),³ Tidwell–Mortimer (TM),¹⁰ and the Error-in-Variables-Model (EVM) method.¹¹ The joint confidence region was determined from EVM. The literature available outlines various techniques to determine copolymer composition via elemental analysis.³ Additional techniques include ¹³C- and ¹H-NMR,¹² IR spectroscopy,² and UV spectrophotometry.¹³ In this work, the analysis is done by ¹H-NMR.

EXPERIMENTAL

Reagents

Inhibitors were removed from the monomers by washing with a 5% NaOH solution and subsequently washing with distilled water. The monomers were distilled under reduced pressure and the middle fractions were kept for the reactions.¹⁴ Benzoyl peroxide was used as the initiator and was purified twice via a crystallization process from chloroform by using methanol. The chloroform and methanol were used without purification. All chemicals were obtained from E-MERCK Chemical Co., Inc., Tehran, Iran.

Procedures

The copolymerization reactions were carried out with different mole ratios of styrene and EHA (1 : 9 through 9 : 1) in the presence of benzoyl peroxide. The reactions were done in sealed ampoules that were de-

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TABLE I
Reactivity Ratio Estimation Experimental Results

f_s	F_s	X
Feed fraction styrene	Copolymer fraction styrene	Conversion (%)
0.198	0.361	13.96
0.305	0.454	12.95
0.398	0.560	11.88
0.505	0.601	9.37
0.599	0.673	8.70
0.702	0.728	8.84
0.801	0.832	8.80
0.895	0.896	7.09

TABLE II
Reactivity Ratio Estimates

Method	r_{styrene}	r_{EHA}
Q-e	0.941	0.258
FR	0.926	0.238
IFR	0.981	0.293
ML	0.949	0.275
YBR	0.946	0.279
KT	0.951	0.276
EKT	0.946	0.247
MH	0.944	0.257
TM	0.970	0.285
EVM	0.979	0.292

gassed through freeze-thaw cycles under 0.1 mmHg. The reactions were carried out at $80.0 \pm 0.1^\circ\text{C}$ to low conversions. For these low conversion experiments, the resulting polymer remains dissolved in the reaction mixture. The polymer was further dissolved with minimal amounts of chloroform and precipitated with methanol. The procedure was carried out three times. The resulting mass of polymer was dried in a vacuum oven at 0.1 mmHg and 50°C until constant weights were achieved. The conversion levels were measured via gravimetric techniques.

Copolymer characterization: $^1\text{H-NMR}$ spectroscopy

$^1\text{H-NMR}$ spectra were recorded by using a Bruker FT-NMR AC 80 A spectrometer. The composition was

determined from the $^1\text{H-NMR}$ spectra of the samples by using standard techniques.

RESULTS AND DISCUSSION

Reactivity ratio estimation experiments

The results from the reactivity ratio experiments are presented in Table I. This table shows the copolymer composition along with the feed composition and conversion levels.

Figure 1 details the behavior of the system via a plot of the copolymer composition versus feed composition. It is evident from the plot that the system shows azeotropic behavior at high feed fractions of styrene.

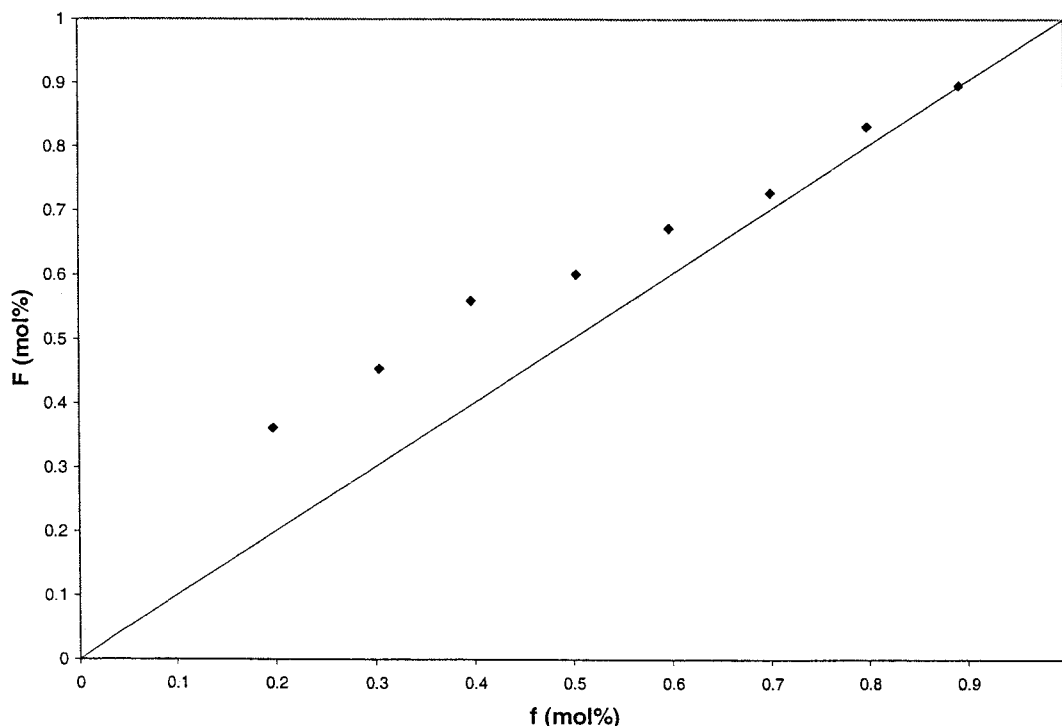


Figure 1 Copolymer composition (f) versus feed composition (f) [mol % styrene].

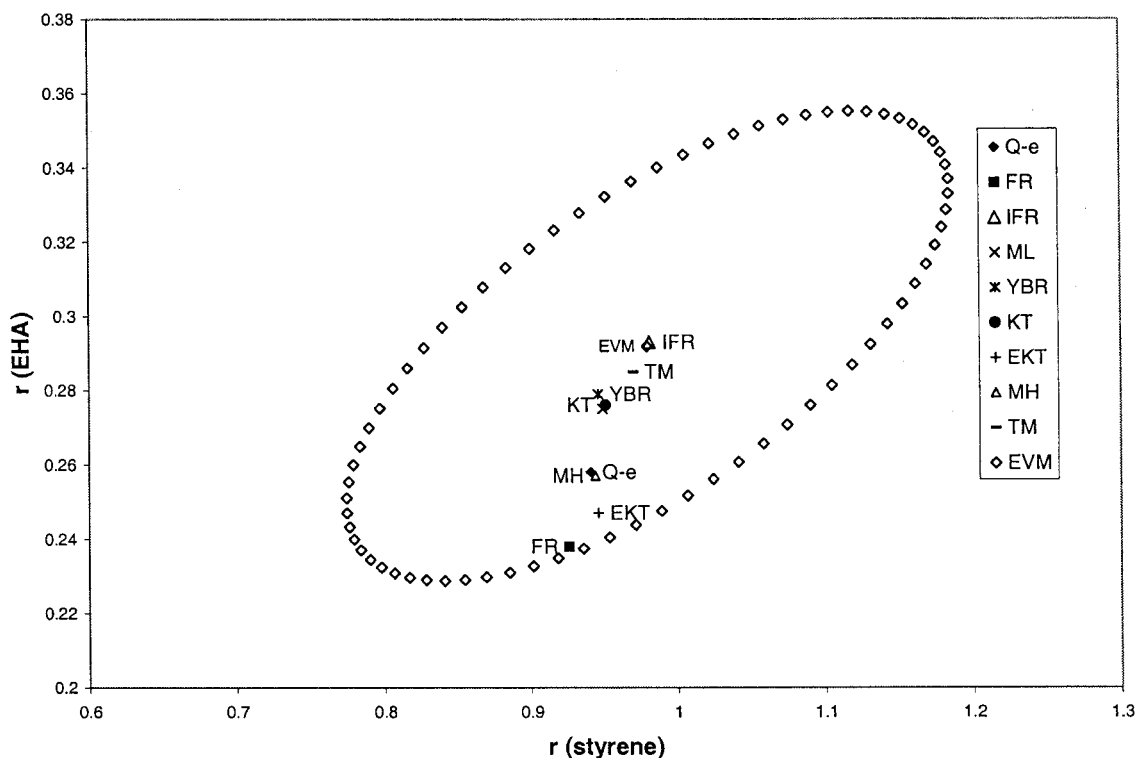


Figure 2 Reactivity ratio estimates with 95% confidence interval generated by EVM.

This behavior is also seen with other styrene–acrylic copolymers at similar feed compositions.¹⁵

Reactivity ratio estimates

The reactivity ratios (based upon the data in Table I) can be estimated from the techniques mentioned earlier. The majority of these techniques are in fact linearized models that may often provide adequate point estimates, but do not retain the error structure associated with the original model. EVM, on the other hand, is a nonlinear technique based on the correct structure of the model, which also provides joint confidence regions.¹¹ Table II summarizes the reactivity ratio estimates from the different methods. From the EVM reactivity ratio values, the azeotrope of the system can be calculated to be $f(\text{styrene}) = 0.972$.

Figure 2 summarizes the data points above including the 95% joint confidence region generated by the EVM method. It shows that all of the point estimates fall within the region indicated but some techniques are certainly better conditioned than others. There is an obvious scatter of the estimates, with IFR, TM, KT, and YBR being closer to the point estimate from EVM.

CONCLUSION

Reactivity ratios were estimated at 80°C for styrene–EHA copolymerization by using several estimation techniques. The EVM values are $r_s = 0.979$ and $r_{\text{EHA}} =$

0.292. The azeotrope for the system is calculated to be $f(\text{styrene}) = 0.972$. The product of the reactivity ratios is less than 1, leaning toward an alternating copolymerization, whereas there is a tendency for styrene to be selectively incorporated relative to EHA.

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