Monomer reactivity ratios of styrene–4-vinylpyridine copolymers at low and high conversions

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Monomer reactivity ratios in free-radical copolymerization of styrene and 4-vinylpyridine monomers at 80°C in toluene solution under reduced pressure were determined for low and high conversions. Finemann–Ross, Kelen–Tüdös, extended Kelen–Tüdös and Mayo–Lewis methods were used for this purpose. The most reliable method was found to be the extended Kelen–Tüdös method. By the use of this method, for conversions below 20%, monomer reactivity values of 0.700 ± 0.005 and 0.335 ± 0.001 were calculated for 4-vinylpyridine and styrene respectively. For conversions greater than 20%, these values were found to reduce to 0.538 ± 0.004 and 0.277 ± 0.001 respectively.

(Keywords: styrene; 4-vinylpyridine; monomer reactivity ratio; copolymerization)

INTRODUCTION

Monomer reactivity ratios are important quantitative values to predict the copolymer composition for any starting feed and to understand the kinetic and mechanistic aspects of copolymerization. For this reason, in the last two decades, a vast amount of data on reactivity ratios has accumulated in the literature. The results obtained for the same systems by different methods or by different investigators are usually inconsistent with each other. Detailed studies investigating the merits of various methods and making comparisons among them are needed to find out the best way of determining reactivity ratios.

Monomer reactivity ratios are generally determined at low conversions. 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 provide experimental evidence that monomer reactivity ratios are not independent of conversion under certain conditions[3–5]. The change in reaction medium with conversion affects the monomer reactivity ratio values.

Among several methods available to determine monomer reactivity ratio values[6–13], the Finemann–Ross (FR)[7], Yezrielev–Brokhina–Roskin (YBR)[8] and Kelen–Tüdös (KT)[9] methods are appropriate for the determination of monomer reactivity ratios at low conversions. The Mayo–Lewis (ML)[1] and extended Kelen–Tüdös (EKT)[10–12] methods consider the drift in the comonomer and copolymer compositions with conversion. Therefore, they are suitable for the manipulation of high-conversion data.

In this study, the monomer reactivity ratios of styrene and 4-vinylpyridine for their free-radical copolymerization were determined 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. Joint confidence limits for each method have been calculated as well. In these respects, this is a more detailed study than the ones available in the literature on the monomer reactivity ratios of styrene and 4-vinylpyridine monomers[14–16].

EXPERIMENTAL

Materials

Toluene, 2-butanone, chloroform, 2-propanol and 1,4-dioxane were supplied by Merck AG, and were used without any further purification.

Petroleum ether was supplied by Birka and was distilled before use. The fraction boiling at 60°C was taken.

Benzoyl peroxide, NaOH and Na_2CO_3 were supplied by Merck AG and were used without any further purification.

Styrene was supplied by Petkim AS. It was treated with NaOH and washed with water several times to remove the inhibitor. Then, it was distilled under reduced pressure over CaH_2. The middle fraction was collected.

4-Vinylpyridine supplied by Merck AG was distilled under reduced pressure before use. The middle fraction was collected.

Copolymerization

The copolymerization was carried out under reduced pressure in 20% toluene solution using benzoyl peroxide

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as the initiator. Sets of samples with approximately equal compositions but with different molecular weights were obtained by varying the weight fraction of the initiator as 0.2, 0.5, 1.0 and 2.0% (w/w) for sets B, A, C and D respectively. The polymerization times changed between 20 and 120 min.

The polymers obtained were dissolved in chloroform, precipitated in petroleum ether, redissolved in 2-butanol and reprecipitated in petroleum ether. The gummy polymers obtained were freeze-dried from their 1,4-dioxane solutions and dried under reduced pressure for several days.

Copolymer compositional analysis

Compositional analyses of the copolymers with respect to the mole fraction of 4-vinylpyridine in the copolymer were determined by: (i) micro-Kjeldahl analysis; (ii) elemental analysis using a Hewlett–Packard model 185 C, H, N analyser; (iii) ^1H n.m.r. spectrometry using a Bruker AC 80 MHz model n.m.r. spectrometer as described in refs. 16 and 17; and (iv) infra-red spectrometry using a Nicolet FFT-510 model *FT*-i.r. spectrometer, by following the peak at 1418 cm^{-1}.

RESULTS AND DISCUSSION

Copolymerization and copolymer compositional analysis

The copolymerization data for low (<20%) and high (>20%) conversions are given in *Tables 1* and *2* respectively.

Table 1 Synthesis of styrene–4-vinylpyridine copolymers (low-conversion data)

Sample	f_1	f_2	F_1	w_1	w_2	w_p	Conv. (%)
A1	0.042	0.736	0.12	0.347	6.101	0.895	9.1
B1	0.040	0.736	0.12	0.334	6.112	0.587	13.9
C1	0.042	0.736	0.12	1.067	18.472	3.388	17.3
A2	0.096	0.682	0.23	0.831	5.837	1.306	19.6
B2	0.094	0.679	0.25	0.784	5.351	0.689	11.2
B3	0.200	0.578	0.35	1.669	4.797	0.708	11.0
B4	0.271	0.501	0.44	2.258	4.133	0.877	13.7
A5	0.386	0.390	0.54	3.269	3.281	1.607	20.0
B5	0.392	0.384	0.55	3.309	3.209	0.938	14.4
A6	0.505	0.271	0.67	4.226	2.246	0.799	12.3
B6	0.502	0.270	0.71	4.215	2.250	0.788	12.1

f_1, f_2 = initial mole fractions of 4-vinylpyridine and styrene
F_1 = mole fraction of 4-vinylpyridine in the copolymer
w_1, w_2, w_p = weights of 4-vinylpyridine, styrene and polymer respectively

Table 2 Synthesis of styrene–4-vinylpyridine copolymers (high-conversion data)

Sample	f_1	f_2	F_1	w_1	w_2	w_p	Conv. (%)
C2	0.101	0.681	0.18	2.607	17.396	6.103	50–60
C3	0.199	0.583	0.30	5.162	14.967	9.859	50–60
C4	0.278	0.505	0.38	7.216	13.018	7.204	50–60
C5	0.398	0.586	0.48	10.433	10.010	16.894	50–60
C6	0.491	0.296	0.62	13.096	6.899	15.687	50–60
D1	0.043	0.718	0.13	0.339	5.682	1.446	24.0
D2	0.104	0.767	0.24	0.853	6.236	2.077	29.3
D3	0.201	0.569	0.35	1.660	4.645	2.778	44.1
A3	0.191	0.588	0.35	1.621	4.951	1.554	23.7
D4	0.282	0.488	0.45	2.316	3.975	2.312	36.8
A4	0.256	0.522	0.43	2.191	4.425	1.607	24.2
D5	0.395	0.374	0.55	3.270	3.076	1.515	23.9
D6	0.519	0.248	0.70	4.257	2.022	1.515	24.1

Table 3 Composition analyses of the samples with respect to the mole fraction of 4-vinylpyridine in the copolymer

Sample	Kjeldahl	Elemental analysis	*FT*-i.r.	^1H n.m.r.	Average
A1	–	0.13	–	0.11	0.12
B1	–	0.14	–	0.10	0.12
C1	0.09	0.11	0.15	–	0.12
D1	–	0.13	–	0.13	0.13
A2	–	0.23	–	0.23	0.23
B2	–	0.27	–	0.23	0.25
C2	0.18	0.17	0.20	0.17	0.18
D2	–	0.26	–	0.22	0.24
A3	–	0.36	–	0.33	0.35
B3	–	0.36	–	0.35	0.35
C3	0.29	0.34	0.30	0.30	0.30
D3	–	0.35	–	0.34	0.35
A4	–	0.42	–	0.44	0.43
B4	–	0.45	–	0.44	0.44
C4	0.35	0.34	0.42	0.39	0.38
D4	–	0.45	–	0.46	0.45
A5	–	0.57	–	0.54	0.55
B5	–	0.57	–	0.54	0.55
C5	0.47	0.44	0.49	0.51	0.48
D5	–	0.56	–	0.55	0.55
A6	–	0.67	–	0.67	0.67
B6	–	0.71	–	0.70	0.71
C6	0.61	0.55	0.68	0.63	0.62
D6	–	0.64	–	0.76	0.70

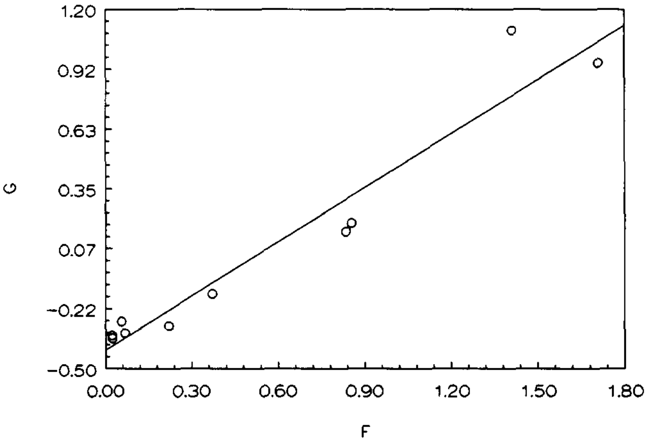

Figure 1 Finemann–Ross plot

The compositions of the samples with respect to the mole fraction of 4-vinylpyridine in the copolymer are given in *Table 3*.

Monomer reactivity ratios

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

$$G = r_1 F - r_2 \tag{1}$$

where:

$$G = X(Y-1)/Y \qquad F = X^2/Y$$

$$X = f_1/f_2 \qquad Y = F_1/F_2$$

The inverted FR equation gives r_1 as the intercept and r_2 as the slope:

$$G/F = -r_2(1/F) + r_1 \tag{2}$$

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

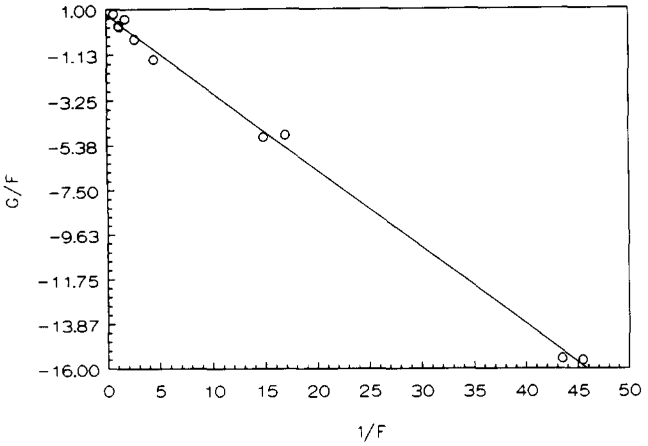

Figure 2 Inverted Finemann–Ross plot

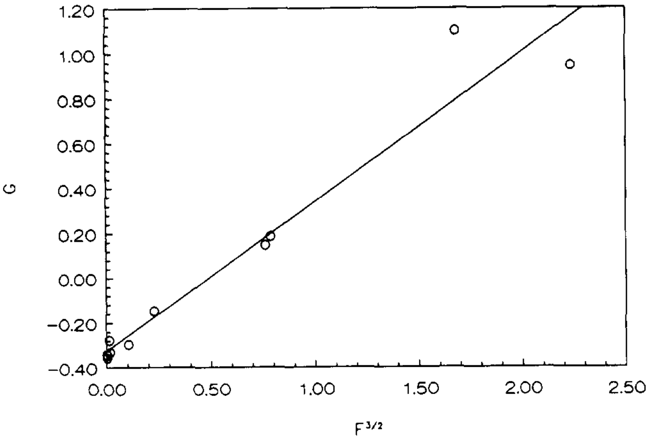

Figure 3 Yezrielev–Brokhina–Roskin plot

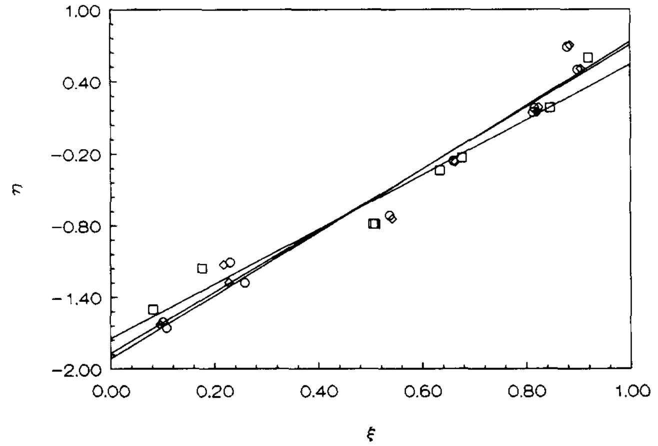

Figure 4 Kelen–Tüdös plot (○, low conversion) and extended Kelen–Tüdös plots (◇, low conversion; □, high conversion)

The YBR equation is another derivative of the FR equation:

$$G/F^{0.5} = r_1 F - r_2(1/F^{0.5}) \tag{3}$$

The YBR plot is given in *Figure 3*.

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

$$\eta = (r_1 + r_2/\alpha)\xi - r_2/\alpha \tag{4}$$

where:

$$\eta = G/(\alpha + F) \qquad \xi = F/(\alpha + F)$$

The intercepts at $\xi = 0$ and $\xi = 1$ of the η *versus* ξ plot gives $-r_2/\alpha$ and r_1 respectively. The KT plot for the low-conversion data of this system is given in *Figure 4*.

The effect of conversion is considered in the extended Kelen–Tüdös equation:

$$F = (F_1/F_2)/[(\log z_1)/(\log z_2)]^2 \tag{5}$$

$$G = (F_1/F_2 - 1)/[(\log z_1)/(\log z_2)] \tag{6}$$

where $z_1 = f_{1,f}/f_{1,0}$, $z_2 = f_{2,f}/f_{2,0}$ and $f_{1,0}$, $f_{1,f}$, $f_{2,0}$ and $f_{2,f}$ are initial and final mole fractions of monomers 1 and 2, respectively. The partial molar conversion of monomer 2 is defined as:

$$\zeta_2 = w(\mu + X)/(\mu + Y) \tag{7}$$

where w = weight conversion of polymerization, and μ = ratio of molecular weight of monomer 2 to that of monomer 1. The partial molar conversion of monomer 1 is:

$$\zeta_1 = \xi_2(Y/X) \tag{8}$$

Then:

$$Z = \log(1 - \zeta_1)/\log(1 - \zeta_2) \tag{9}$$

where:

$$F = Y/Z^2 \qquad G = (Y - 1)/Z$$

$$\eta = G/(\alpha + F) \qquad \xi = F/(\alpha + F)$$

Extended Kelen-Tüdös plots for low- and high-conversion samples are given in *Figure 4*.

Reactivity values were calculated by the ML method using the integrated copolymerization equation with the aid of a computer[18]. The ML plot for high-conversion copolymerization of styrene and 4-vinylpyridine is given in *Figure 5*.

In all of these calculations, 4-vinylpyridine has been considered as monomer 1 and styrene as monomer 2. Consequently, r_v and r_s values given in the figures and tables correspond to r_1 and r_2 values respectively in the equations given above.

The monomer reactivity ratio values of 4-vinylpyridine and styrene (r_v and r_s respectively) obtained by various methods are given in *Table 4*.

Among low-conversion methods, the KT method is better than the FR and YBR methods, since proper choice

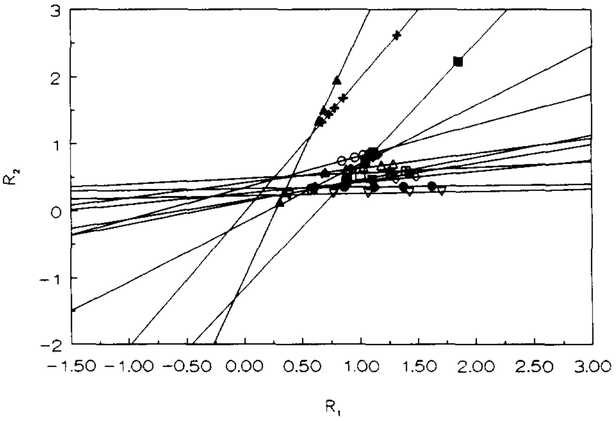

Figure 5 Mayo–Lewis plot (high conversion)

Table 4 Results of monomer reactivity ratio calculations by various methods

Method	r_v	r_s
Lower conversion (<20%)		
Finemann–Ross	0.85	0.41
Finemann–Ross (inverted form)	0.79	0.36
YBR	0.89	0.38
Kelen–Tüdös	0.729 ± 0.01	0.368 ± 0.002
Extended Kelen–Tüdös	0.700 ± 0.005	0.335 ± 0.001
Mayo–Lewis	0.79 ± 0.10	0.36 ± 0.03
Higher conversion (>20%)		
Extended Kelen–Tüdös	0.538 ± 0.004	0.277 ± 0.001
Mayo–Lewis	0.74 ± 0.11	0.35 ± 0.06

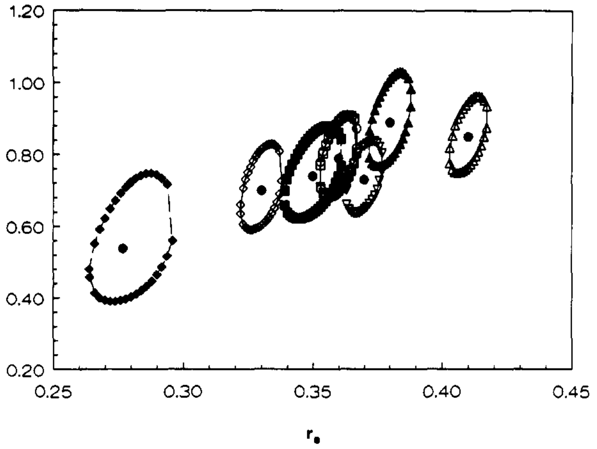

Figure 6 Joint confidence limits (low conversion: △, FR; ○, inverted FR; ▲, YBR; ▽, KT, ◇, EKT; □, ML; high conversion: ◆, EKT; ■, ML; ●, experimental)

of the α value provides a method for uniform distribution of the data in the interval (0, 1). Another advantage of the KT method is that it provides statistical confidence interval calculations and the quantitative evaluation of the confidence in experimental design[12]. An important drawback related to the FR method is that it is subject to re-indexing errors[19–21].

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, much 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 Mayo–Lewis method, which is based on the integrated copolymerization equation, requires tedious calculations, which cannot be carried out without the use of a computer. Furthermore, determination of the intersection point of experimental results brings in extra error to the results, whether it is determined visually or by calculation.

The extended Kelen–Tüdös method allows the calculation of reactivity ratio values without exceeding 0.5% error for a system with $r_1 = 1$, $r_2 = 0.1$ and $x_0 = F_1/F_2 = 1.667$ up to conversions of 60%, while the conventional methods cited above allow only a conversion of 5% for the same system for 0.5% error[10–12].

When results obtained by EKT and ML methods are compared with each other, an important difference between the r_v values is observed for high-conversion data. The value obtained by the EKT method is considered to be the more reliable one owing to the uncertainty related to calculating the best intersection point of the lines in the ML method and the advantages of the EKT method discussed above.

Calculation of the joint confidence intervals

Joint confidence limits of reactivity ratio values for each method have been calculated with the aid of a computer program. The details can be found elsewhere[21,22]. The plots are given in *Figure 6*.

Calculation of the joint confidence limits rather than simple limits of precision is necessary because reactivity ratio estimations are made simultaneously. Therefore, they should not be considered statistically independent. The correct values of the reactivity ratios lie within the joint confidence limits.

Effect of conversion on the reactivity ratio values

It has been observed that the monomer reactivity ratio values show a decrease at high conversions, considering the results obtained by the EKT method. There is a decrease in r_v value from 0.700 and 0.538 and in r_s from 0.335 to 0.277.

A similar observation has been made for the high-conversion copolymerization of styrene and methyl methacrylate monomers[3]. In that study, the decrease in the reactivity ratio value of styrene in a poor solvent or in bulk with the onset of autoacceleration was attributed to a steric effect restricting the mobility of styrene-ended species especially in a highly viscous medium.

There is another study related to these monomers suggesting that reactivity ratios may not be just simple ratios of propagation constants[4].

Reactivity ratios are inherent values of the molecules and should not be affected by the medium of copolymerization. This decrease might be related to an increasing radical stabilization of the growing chain by the penultimate units with increasing conversion. There is evidence in the literature about the general existence of a penultimate unit effect in radical polymerizations[23]. However, the probability that there might be an effect of drift in comonomer and copolymer compositions with conversion, or a decrease in diffusion abilities of the species after the autoacceleration point, in a poor solvent should not be underestimated.

Comparison of the results with those of other workers

Table 5 summarizes the r_v and r_s values calculated for this system in different studies. The low-conversion values of r_v are in accordance with each other. The reactivity

Table 5 Reactivity ratio values reported for the free-radical copolymerization of styrene and 4-vinylpyridine

r_v	r_s	Method	Medium	Ref.
0.52 ± 0.06[a]	0.62 ± 0.02[a]	ML	80°C, toluene	14
(1.035)	(−0.742)	KT		23
0.70 ± 0.1	0.54 ± 0.03	FR	60°C, bulk	15
(0.694)	(0.517)	KT		23
0.75 ± 0.03	0.57 ± 0.03	KT	50°C, benzene	16
0.700 ± 0.005	0.335 ± 0.001	EKT	80°C, toluene	This work
0.538 ± 0.004[a]	0.277 ± 0.001[a]	EKT	80°C, toluene	This work

[a] High-conversion values

ratio value of 0.52 obtained at high conversions by Fuoss and Cathers[14] agrees with our r_v value of 0.538 under very similar conditions. This supports the idea that reactivity ratios change with conversion for the styrene/4-vinylpyridine system. Values of r_s available in the literature differ significantly from the r_s value of 0.335 calculated in this study for conversions of 9–20%. This justifies the importance of determining monomer reactivity ratio values under different experimental conditions.

CONCLUSIONS

The extended Kelen–Tüdös method is a good method for the determination of the monomer reactivity ratios since it considers the effect of conversion on the comonomer and copolymer compositions. The monomer reactivity ratio r_v value calculated for 4-vinylpyridine is in accordance with the calculations of other workers. However, the r_s value of styrene is somewhat less than those calculated by previous workers. The monomer reactivity ratios for this system show a tendency to decrease with increasing conversion, most probably due to a decrease in the diffusion abilities of the species, especially the growing chains, in the toluene solution which is a poor solvent for this system.

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