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Reactivity Ratios for Divinylbenzene and Ethylene Glycol Dimethacrylate Copolymerizations with Styrene and Methyl Methacrylate

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The free radical copolymerization of styrene and other vinyl monomers to produce cross-linked, network polymers is of technological importance in the production of ion-exchange resins, packings for gas-liquid and gel permeation chromatography, cross-linked latex polymers, and other products. The principal multifunctional cross-linking monomers which are used in this connection are ethylene glycol dimethacrylate and divinylbenzenes, and accurate values for reactivity ratios in their reactions with bifunctional monomers are essential for the design of copolymerization processes and products.

Wiley and co-workers have reported reactivity ratios for the copolymerizations of these monomers with styrene and with methyl methacrylate [1]. In these studies the reactivity ratios were calculated from the raw data using a graphical "method of intersections" [2]. In this procedure the differential copolymer equation is put into the form

$$r_2 = \frac{[M_1]}{[M_2]}\left[\frac{d[M_2]}{d[M_1]}\left[1 + \frac{[M_1]}{[M_2]} r_1\right] - 1\right] \qquad (1)$$

where $[M_i]$ and $d[M_i]$ are the concentrations of monomer i in the feed and copolymer, respectively, and the reactivity ratios r_1 and r_2 have their usual meanings [3]. Corresponding experimental values of $[M_1]$, $[M_2]$, $d[M_1]$, and $d[M_2]$ are substituted into Eq. (1) and r_2 is plotted as a function of assumed values of r_1. Each experiment yields one straight line in the r_1r_2 plane, and the intersection region of such lines from different feed compositions is assumed to give the best values of r_1 and r_2. Although this method has been widely used, it suffers from the severe defect that the intersection point which corresponds to the "best" values of r_1 and r_2 is selected subjectively and imprecisely. Each experiment yields a straight line and each such line can intersect the line from every other experiment. Thus n experiments yield n(n - 1)/2 intersections and even one "wild" result produces (n - 1) unreliable intersections.

There is no basis a priori for eliminating suspect values in the method of intersections procedure. Some of the replicate studies reported by Wiley [1] give reactivity ratios which are not consistent with others, and it is not clear which values should be assumed in such cases.

The difficulties with this calculation procedure and other contemporaneous graphical solutions to the simple copolymer equation have been explained by Tidwell and Mortimer [4, 5]. These procedures are arithmetically sound but statistically incorrect because the error structures are not normally distributed and the errors in individual reactivity ratios are coupled. The most generally useful method and the only statistically correct procedure for calculating reactivity ratios from binary copolymerization data involves nonlinear least squares analysis of the data. Computer programs for this purpose are available [5, 6].

Because of the practical importance of these particular reactivity ratios, it appeared worthwhile to reexamine the available experimental data with the aid of the computer-assisted techniques which are now at hand. Recalculated reactivity ratios are reported here and compared with the values given in the initial studies. Joint confidence limit loops have been computed to permit the objective selection of the best values for the different copolymerizing pairs.

Table 1 lists the recalculated and initial reported values for the various reactivity ratios. The reactivity ratios reported for all copolymerizations with methacrylate comonomers have not been significantly altered from the original computations. There are quite large differences in some of the divinylbenzene reactions, however [cf. entries (e), (g), and (h) in Table 1].

Confidence limit loops are instructive in selecting the "best" reactivity ratio values for the various binary copolymerizations. The

TABLE 1. Reactivity Ratios

	r_1		r_2			
Monomer pair[a]	This work	Initial report	This work	Initial report	Temperature (°C)	% conversion
(a) S/EGDM	0.40	0.40 [7]	0.63	0.64 [7]	60	3-4
(b) S/m-DVB	0.62	0.65 [7]	0.55	0.60 [7]	100	3-4
(c) S/m-DVB	0.74	0.61 [8]	1.03	0.88 [8]	80	2-4
(d) S/m-DVB	1.26	1.27 [8]	1.05	1.08 [8]	80	3-8
(e) S/m-DVB	0.59	1.11 [9]	0.50	1.00 [9]	75	4.7-35
(f) MMA/m-DVB	0.43	0.41 [10]	0.62	0.61 [10]	70	3.0-6.5
(g) S/-p-DVB	0.20	0.15 [7, 8]	0.99	0.50 [7, 8]	100	3-4
(h) S/-p-DVB	0.91	0.77 [8]	3.17	2.08 [8]	80	0.5-2
(i) S/-p-DVB	0.56	0.77 [11]	1.33	1.46 [11]	70	2-5
(j) S/-p-DVB	0.17	0.20 [9]	0.76	1.00 [9]	75	2-20
(k) MMA/-p-DVB	0.11[b]	0.10 [10]	0.85[b]	0.93 [10]	70	1-3
(l) S-mDVB	0.62	-	0.54	-	75-100	-
(m) S-pDVB	0.30	-	1.02	-	70-100	-

[a] Monomer 1 is listed first. S = styrene, EGDM = ethylene glycol dimethacrylate, DVB = divinylbenzene, MMA = methyl methacrylate.

[b] These values were calculated using all the experimental data. Reference 10 lists $r_1 = 0.62$, $r_2 = 1.3$ after neglecting two extreme sets of experimental values.

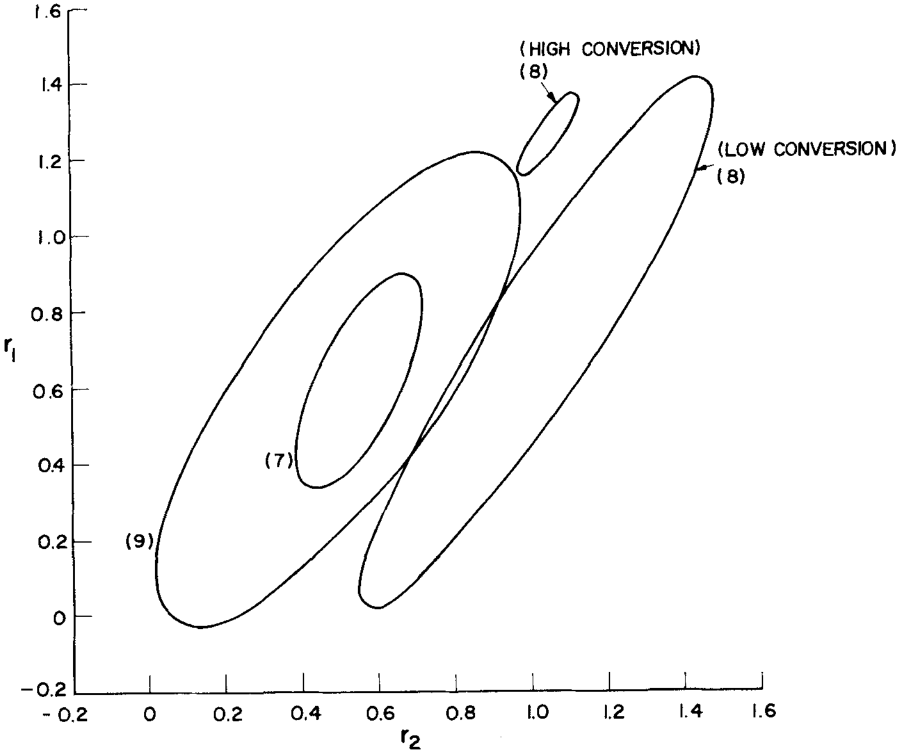

FIG. 1. Approximate 95% joint confidence limits for styrene/m-divinylbenzene copolymerizations. The numbers refer to the references in this article which are the sources of raw data for these calculations.

plots shown are approximate 95% confidence limits for the r_1r_2 pair. These have been calculated by a method [6] similar in principle to that described by Tidwell and Mortimer [5]. In essence, the pair of reactivity ratios can be assumed with 95% confidence to lie somewhere in the loop shown in r_1r_2 space.

Figure 1 shows the confidence limit loops for the styrene/m-divinylbenzene reactions. The values from Refs. 7 and 9 [entries (b) and (e) in Table 1] are mutually consistent, while those from Ref. 8 [entries (c) and (d)] appear to be significantly different. The experiments in Ref. 8 were performed under different experimental conditions and with a different analytical technique. We are inclined to reject the values from Ref. 8 as being subject to error for reasons which are not now assignable. The compatible sets or r_1 and r_2 values are from reaction temperatures which bracket that of the suspect reactivity ratios.

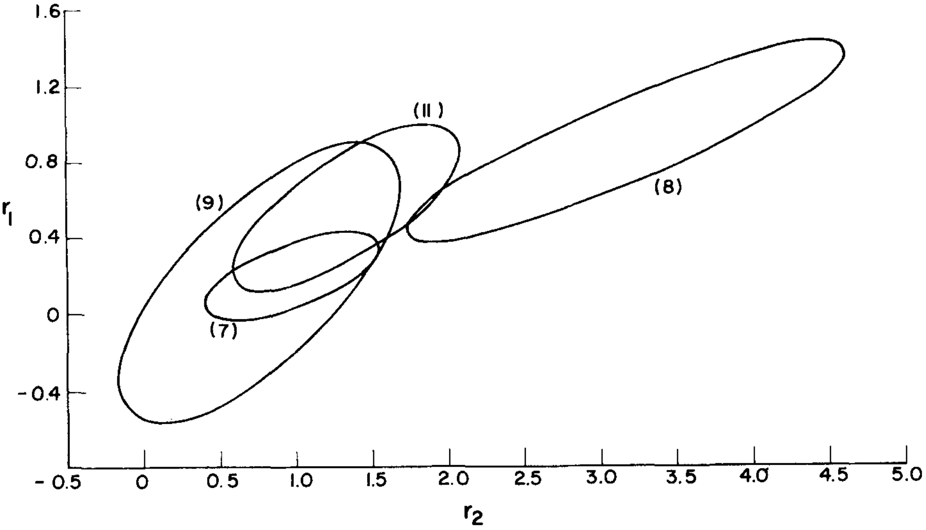

FIG. 2. Approximate 95% joint confidence limits for styrene/p-divinylbenzene copolymerizations. The labels on the curves refer to the references in this article which are the sources of raw data for these calculations.

The latter consist themselves of two sets obtained at slightly different total monomer conversions. These r_1r_2 pairs are not mutually consistent at the 95% confidence level, as shown in Fig. 1. Also, the higher conversion data yield r_1 and r_2 both > 1. This has not been observed heretofore in free radical copolymerizations and is doubtful because it implies block copolymer formation which is not expected from the chemical natures of the reactants. Further, the data from this reference are also in disagreement with previous results for p-divinylbenzene copolymerizations, as shown below.

The reactivity ratios from Ref. 7 appear to be the most plausible set in this series of measurements. The confidence limit loop for these data nests within that of Ref. 9. The values themselves [r_1 (styrene) = 0.62, r_2 = 0.55] are reasonable. The confidence limit loops also encompass joint pairs like r_1 = 0.9, r_2 = 0.7, which are closer to the "ideal" behavior which might be expected from the similarity of the comonomers.

Figure 2 is a similar plot for the styrene/p-divinylbenzene copolymerizations. The data from Ref. 8 again do not have the consistency which was found in the other studies, which include Refs. 7, 9, and 11 in this case. The confidence limit loop from Ref. 7 again nests within those of the other two reports. These seem to be the preferred data, again.

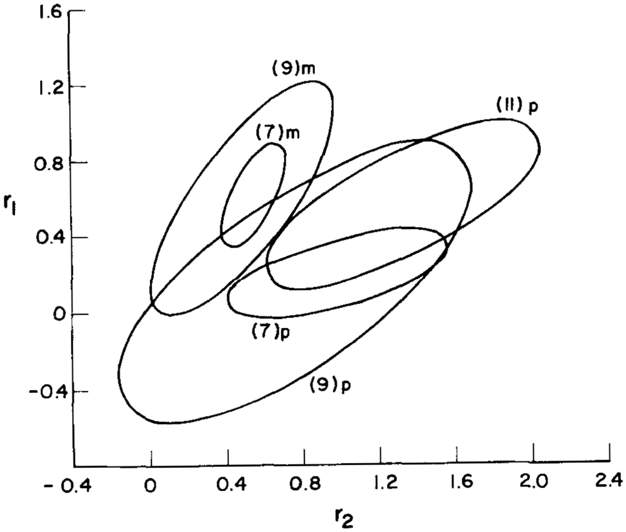

FIG. 3. Approximate 95% confidence limits for copolymerizations of styrene with p-divinylbenzene (labeled p) and m-divinylbenzene (labeled m). The numbers on the curves refer to the reference numbers in this article.

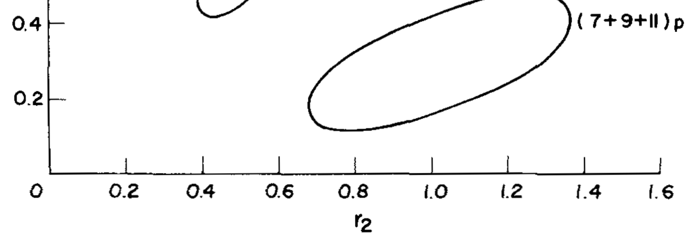

FIG. 4. Approximate 95% confidence limits for copolymerizations of styrene with p-divinylbenzene (labeled p) and m-divinylbenzene (labeled m) for the amalgamated raw data sets. The numbers on the curves refer to the reference numbers in this article.

Figure 3 superimposes the joint confidence limits for all copolymerizations of styrene with both divinylbenzenes. The data from Ref. 8 have been excluded for clarity of presentation, since they seem to be inconsistent with the results of the other research quoted. The reactivity ratios for the two divinylbenzenes are significantly different at the 95% confidence level.

Finally, we have combined the data sets which seem to be mutually consistent and calculated reactivity ratios and confidence limit loops for the amalgamated raw data. Thus Refs. 7 and 9 yield $r_1 = 0.62$, $r_2 = 0.54$ for styrene/m-divinylbenzene [entry (l) in Table 1] and the results in Refs. 7, 9, and 11 give $r_1 = 0.30$, $r_2 = 1.02$ for styrene/p-divinylbenzene [entry (m) in Table 1]. The two joint confidence limit loops are shown in Fig. 4, where it is clear that the reactivity ratios differ significantly for the two copolymerizations.

The last values quoted are the best figures which can be estimated from the research of Wiley and co-workers.

It should be remembered that these reactivity ratios refer to low conversion reactions of styrene with only one of the two vinyl groups in the multifunctional monomer. The observed differences in gelation characteristics of the two divinylbenzene isomers are consistent with these reactivity ratios, however. Thus r_2 for the para isomer is greater than that for m-divinylbenzene (styrene is monomer 1). At equal total monomer conversion and initial feed composition, a styrene/p-divinylbenzene reaction will yield a product with more enchained divinyl monomer and higher functionality for further polymerization. The para isomer does in fact show a lower conversion at gelation [1].

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