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### Monomer Reactivity Ratios for the Copolymerization of Styrene with Pure Meta-and Pure Para-Divinylbenzenes

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## Monomer Reactivity Ratios for the Copolymerization of Styrene with Pure Meta- and Pure Para-Divinylbenzenes

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### Summary

Reactivity ratios for the copolymerization of styrene ( $r_1$ ) meta-divinylbenzene ( $r_2 - m$ ) and with para-divinylbenzene ( $r_2 - p$ ) have been redetermined under different reaction conditions and with different radioactivity assay techniques. The copolymers were prepared at two conversion levels [0.55 to 3.7% and 2.7 to 7.5% and at 80° (rather than 100°)] with benzoyl peroxide (in place of *t*-butylhydroperoxide) initiator. The ionization chamber-vibrating reed electrometer radioactivity assay technique developed for other copolymerization studies was used in place of the direct counting technique previously used for the styrene/divinylbenzene systems. The new values are  $r_1 = 0.605/r_2 - m = 0.88$ ;  $r_1 = 0.77/r_2 - p = 2.08$  at 0.55 to 3.7% conversion and  $r_1 = 1.27$ ;  $r_2 - m = 1.08$  at 2.7 to 7.5% conversion. These are not in close agreement with previous values partly because of the difference in conditions of copolymerization (temperature, per cent conversion, initiator) and in the improved analytical precision. Also the high-DVB-content (80%) para copolymer data are not assumed to be invalid and are not omitted (as they were before) from selection of the  $r_2 - p$  values.

The new values do, however, show the same type of alternating tendencies. They are also in accord with estimates based on Hückel MO calculations of  $r_1 \cong r_2 - m \cong 1$  and  $r_1 = 0.75/r_2 - p = 1.5$ .

The monomer reactivity ratios for the copolymerization of styrene with meta-divinylbenzene and with para-divinylbenzene are one of the most significant features which distinguish these two divinyl monomers. It was noted as early as 1934 by Staudinger and Heuer (1) that styrene and divinylbenzene polymerizations are kinetically different in qualitative experiments. The first quantitative determinations (2) in 1960 of the reactivity ratios were interpreted to give values of  $r_1 = 0.6$ ,  $r_2 - m = 0.6$  for styrene and the meta isomer; and  $r_1 = 0.15$ ,  $r_2 - p = 0.5$  for styrene and the para isomer. These differences between the copolymerization behavior of the two pairs establish probable structural differences in the resultant cross-linked copolymer network. These differences have been demonstrated in terms of the chemical and physical behavior of the copolymers (3,4). It thus becomes significant that as precise and valid data as it is now possible to obtain be made available for the further development of this structural problem.

The previously recorded values (2) were obtained by a direct counting technique which is less precise than a subsequently developed ionization-chamber technique. We have now repeated the determinations using this latter technique and wish to report our results as part of our program designed to provide a more useful interpretation of such results than has yet been possible, through clarification of some of the assumptions previously involved.

## EXPERIMENTAL

### Monomers

The styrene (DPI) was distilled in vacuo over potassium hydroxide just prior to use. A center cut,  $N_{\text{D}}^{20}$  1.5465 [reported (5)  $N_{\text{D}}^{20}$  1.5465] was used. Styrene-8- $C^{14}$  with specific activity of 0.5 mcuries/mmole stabilized with picric acid (Tracerlab Co., L-2-6, lot 38-273-7) was diluted as previously described to approximately 0.881  $\mu$ curies/mmole. Commercial divinylbenzene (Koppers Co., Sample No. 1053) was fractionated three times by preparative gas chromatography as previously described (6) to give meta-divinylbenzene. This material was twice vacuum distilled to give the sample used

in the copolymerizations,  $N_D^{31.5}$  1.5717. Gas-chromatographic analysis (flame-ionization detector, Perkin Elmer Model 800) indicated this sample to be 99.55% meta and 0.21% para isomers with 0.24% ethylstyrene. The para-divinylbenzene was separated by preparative gas chromatography (7) from a sample of 90% para supplied by Cosden Chemical Co. Gas-chromatographic analysis (flame-ionization detector, Perkin Elmer Model 800) established that this sample was 99.83% para and 0.17% meta isomers. The data are given in Fig. 1.

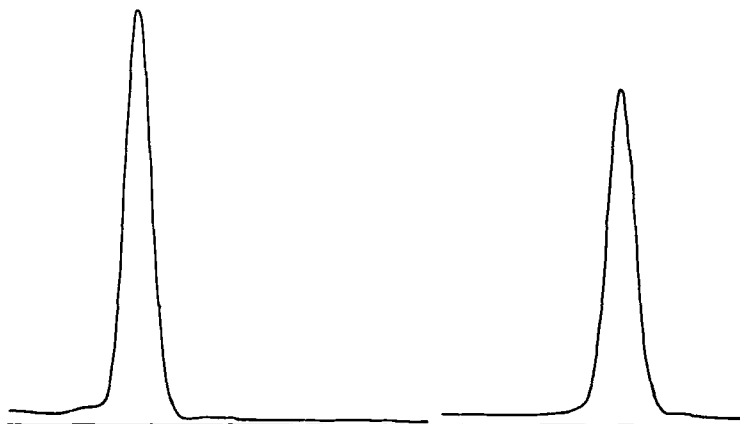


FIG. 1. Gas-chromatographic analysis of meta (left) and para (right) divinylbenzenes. Flame-ionization detector, Ucon LB 550-X on Chromasorb-W support.

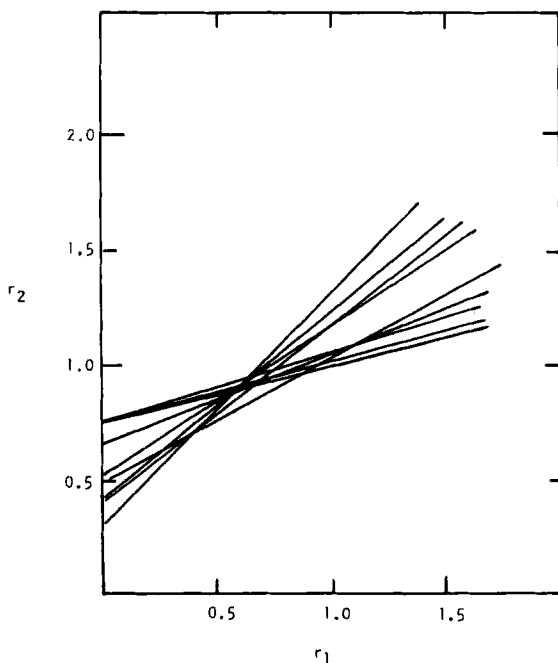
### Copolymerizations

The monomer mixtures were prepared by vacuum-line techniques previously used (8). This involves vacuum transfer of the above-described monomers to a reaction (centrifuge) tube with weights thereof determined by difference. Initiator (benzoyl peroxide, 0.1% by weight of the monomer mixture) was added, the mixture was frozen, degassed, sealed under vacuum, and polymerized at  $80 \pm 0.1^\circ\text{C}$  in an oil bath. The polymerization was stopped by freezing. At the time of analysis and within 24 hr, the copolymer was thawed quickly, suspended in benzene, precipi-

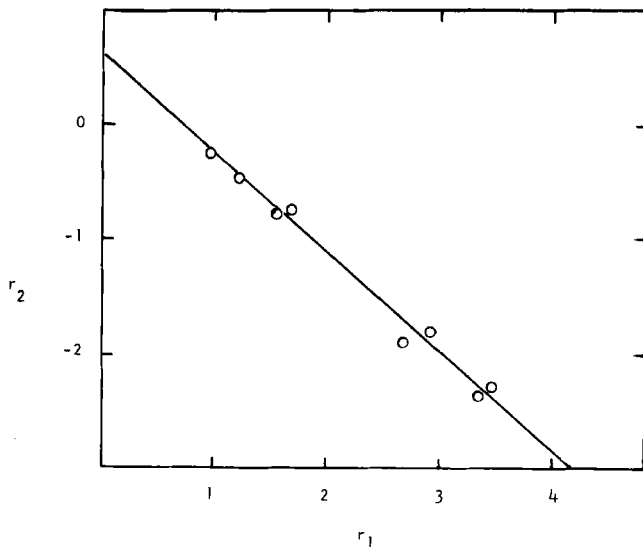
tated by methanol, and collected by centrifugation. The methanol washing was repeated three times and the copolymer was collected and freeze-dried to constant weight in vacuo as previously described (8). The conversions ranged from 0.55 to 3.70% in one series of runs (both meta and para) and from 2.7 to 7.5% in another set of runs (only meta). Each composition was run in duplicate. Complete data for each copolymerization in each series are given in the tables.

### Radioactivity Assay

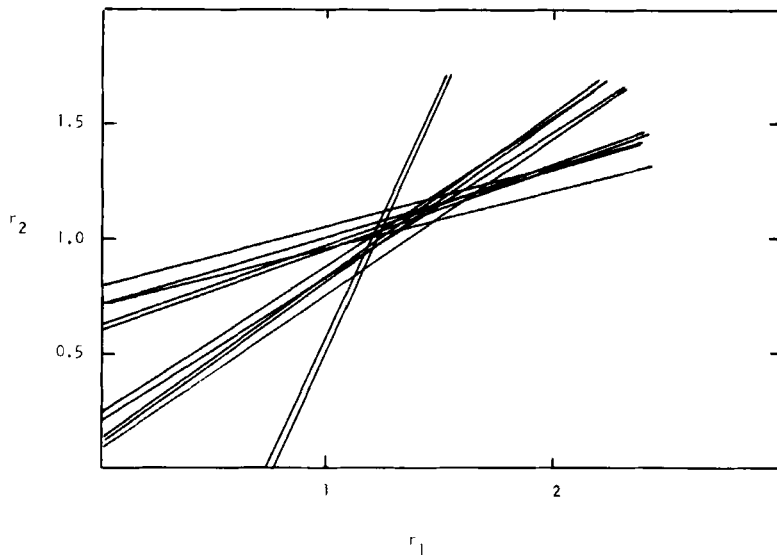
Duplicate analyses were made on duplicate samples of copolymer from duplicate runs using techniques developed by others (9) and used in our previous studies (8). A spherical Borkowski ionization chamber, Cary Model 31 vibrating-reed electrometer, and L and N recorder were used. Analytical data are given in the tables and plotted in the figures.



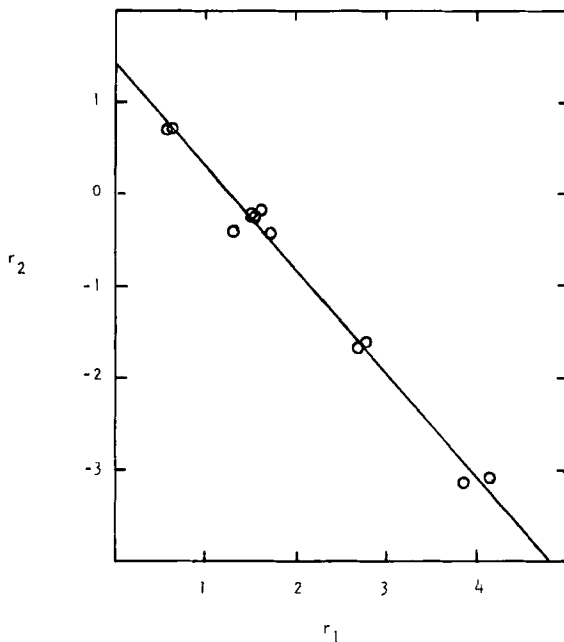
**FIG. 2.** Intersect plot for the copolymerization of styrene ( $r_1 = 0.6$ ) *m*-divinylbenzene ( $r_2 = 0.88$ ) at  $80^\circ$  with benzoyl peroxide initiator. The data are for the duplicate analyses on the copolymers listed in Tables 1 and 2. (Conversion 1.8 to 3.7%.)



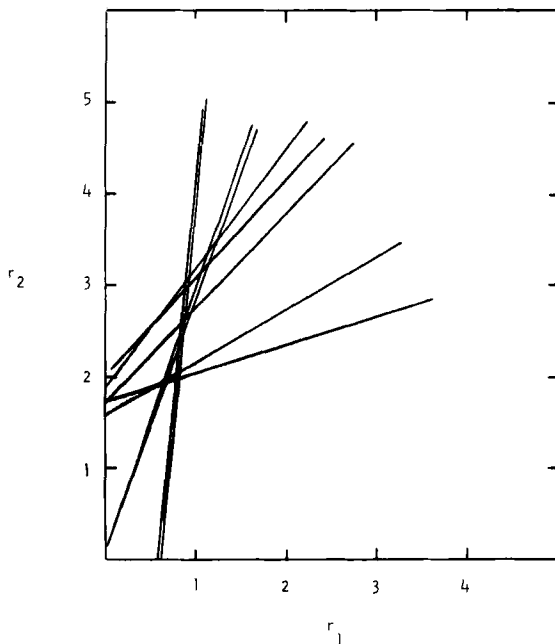
**FIG. 3.** Fineman-Ross plot for the copolymerization of styrene ( $r_1 = 0.605$ ) and *m*-divinylbenzene ( $r_2 = 0.88$ ) at  $80^\circ$  with benzoyl peroxide initiator and at 1.8 to 3.7% conversion. The data are for duplicate analyses on the copolymers listed in Tables 1 and 2 and the line is located by least squares.



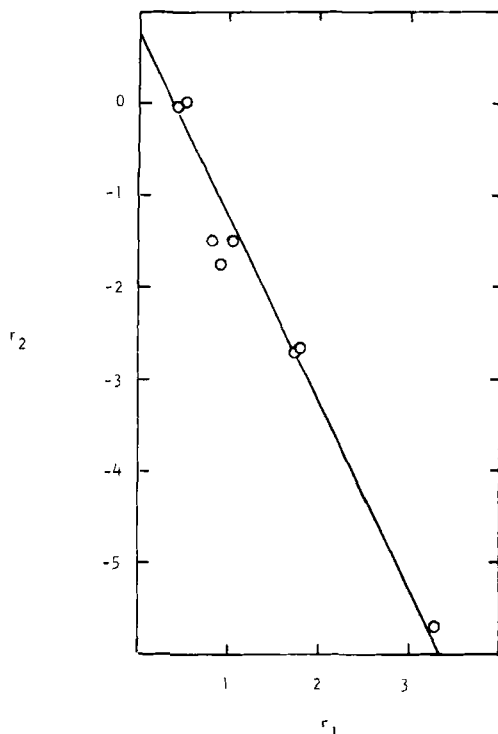
**FIG. 4.** Intersect plot for the copolymerization of styrene ( $r_1 = 1.27$ ) and *m*-divinylbenzene ( $r_2 = 1.08$ ) at  $80^\circ$  with benzoyl peroxide initiator and at 2.7 to 4.96% conversion. The data are for the duplicate analyses on the copolymers listed in Tables 3 and 4.



**FIG. 5.** Fineman-Ross plot for the copolymerization of styrene ( $r_1 = 1.27$ ) and *m*-divinylbenzene ( $r_2 = 1.08$ ) at  $80^\circ$  with benzoyl peroxide initiator and at 2.7 to 4.96% conversion. The data are for duplicate analyses on the copolymers listed in Tables 3 and 4 and the line is located by least squares.



**FIG. 6.** Intersect plot for the copolymerization of styrene ( $r_1 = 0.77$ ) and *p*-divinylbenzene ( $r_2 = 2.08$ ) at  $80^\circ$  with benzoyl peroxide initiator. The data are for the duplicate analyses on the copolymers listed in Tables 5 and 6.



**FIG. 7.** Fineman-Ross plot for the copolymerization of styrene ( $r_1 = 0.77$ ) and *p*-divinylbenzene ( $r_2 = 2.08$ ) at  $80^\circ$  with benzoyl peroxide initiator. The data are for the duplicate analyses on the copolymers listed in Tables 5 and 6 and the line is located by least squares.

## RESULTS AND DISCUSSIONS

The data available from the present study make possible a much more informed analysis of the polymerization of styrene with the two divinylbenzene isomers (meta and para) than has been possible previously. We wish at this time to comment on three aspects of the presently available new data. These are: (1) the precision and accuracy of the data, (2) the previously unappreciated significance of changes in copolymerization conditions and isolation procedures on the apparent reactivity ratio values for the meta isomer, and (3) the indications in the data for para isomer that block copolymerization is involved. The over-all conclusions are consistent with previously established concepts and with theoretical calculations based on Hückel MO calculations.



TABLE 1

Monomer Feed Composition: Copolymerization of Styrene and *m*-Divinylbenzene at 80° (Low-conversion series)

| No. | Monomer feed, g |               | $M_1/M_2$ | Wt.-%   | Wt.-%         | Mole-%  | Conversion,<br>% |
|-----|-----------------|---------------|-----------|---------|---------------|---------|------------------|
|     | Styrene         | <i>m</i> -DVB |           | styrene | <i>m</i> -DVB | styrene |                  |
| 1.  | 0.6638          | 0.4480        | 1.7821    | 58.59   | 41.41         | 64.06   | 3.72             |
| 2/3 | 0.4865          | 0.4208        | 1.4563    | 53.62   | 46.38         | 59.14   | 1.79             |
| 4/5 | 0.3913          | 0.4256        | 1.1581    | 47.90   | 52.10         | 53.66   | 2.03             |
| 6/7 | 0.4319          | 0.6148        | 0.7004    | 35.74   | 64.26         | 41.19   | 2.10             |
| 8/9 | 0.1813          | 0.3872        | 0.5898    | 31.89   | 68.11         | 37.10   | 2.20             |

Comment on the precision and accuracy of the data obtained in this study need not be extensive but it is advisable, we think, to comment on the point as a prelude to the analysis of the data. The technique we are using involves combustion and ionization-chamber counting techniques with a vibrating-reed electrometer technique developed by others (9) as extremely reliable for  $^{14}\text{C}$  research. In our own research using the styrene-methyl methacrylate system as a model, we have established what are confirmed by others (10) as probably the most accurate data yet reported for this copolymerization. In the present study a complete set of copolymers were made and analyzed as practice runs (not reported

TABLE 2

Copolymer Composition: Copolymerization of Styrene and *m*-Divinylbenzene at 80°, Ionization-Chamber Assay (Low-conversion series)

| No. | Sample wt., mg | Specific charge, mv/mg/sec | Wt.-% $m_1$ | Wt.-% $m_2$ | Molar ratio $m_2/m_1$ |
|-----|----------------|----------------------------|-------------|-------------|-----------------------|
| 1   | 6.343          | 1.1087                     | 37.97       | 62.03       | 1.2968                |
| 2   | 1.500          | 0.9931                     | 34.04       | 65.96       | 1.5381                |
| 3   | 4.329          | 1.0182                     | 34.87       | 65.22       | 1.4886                |
| 4   | 5.530          | 0.8970                     | 30.74       | 69.26       | 1.7886                |
| 5   | 5.560          | 0.8527                     | 29.23       | 70.77       | 1.9220                |
| 6   | 2.352          | 0.6080                     | 20.83       | 79.17       | 3.0175                |
| 7   | 2.557          | 0.6390                     | 21.90       | 78.10       | 2.8312                |
| 8   | 2.210          | 0.5471                     | 18.75       | 81.25       | 3.4411                |
| 9   | 1.986          | 0.5628                     | 19.29       | 80.71       | 3.3224                |

TABLE 3

Monomer Feed Composition: Copolymerization of Styrene and *m*-Divinylbenzene at 80° (High-conversion series)

| No.   | Monomer feed, g |               | $M_1/M_2$ | Wt.-%   | Wt.-%         | Mole-%  | Conversion,<br>% |
|-------|-----------------|---------------|-----------|---------|---------------|---------|------------------|
|       | Styrene         | <i>m</i> -DVB |           | styrene | <i>m</i> -DVB | styrene |                  |
| 1/2   | 0.8336          | 0.2129        | 4.9322    | 79.66   | 20.44         | 83.14   | 2.71             |
| 3/4   | 0.3479          | 0.2808        | 1.5605    | 55.34   | 44.66         | 60.94   | 4.96             |
| 5/6   | 0.3315          | 0.2709        | 1.5414    | 55.03   | 44.97         | 60.65   | 4.57             |
| 7/8   | 0.3703          | 0.3461        | 1.3480    | 51.69   | 48.31         | 57.41   | 7.50             |
| 9/10  | 0.2539          | 0.4250        | 0.7525    | 37.40   | 62.60         | 42.94   | 3.09             |
| 11/12 | 0.2671          | 0.6744        | 0.4989    | 28.37   | 71.63         | 33.29   | 4.71             |

herein) for laboratory experience. The meta data given in Tables 1 to 4, and the para data, given in Tables 5 and 6, were then obtained for copolymer compositions prepared in duplicate, each one of which was then assayed in duplicate. For example, Figs. 4 and 5 give the data for 12 such assays for six pairs of copolymer compositions listed in Tables 3 and 4. The  $r_1$  and  $r_2$  values are read directly from intersect plots or determined from the intersect and slope of a least-squares fit of the Fineman-Ross plot.

TABLE 4

Copolymerization of Styrene and *m*-Divinylbenzene at 80°;  
Ionization-Chamber Assay (High-conversion series)

| No. | Sample<br>wt., mg | Specific<br>charge,<br>mv/mg/sec | Wt.-%<br>$m_1$ | Wt.-%<br>$m_2$ | Molar<br>ratio<br>$m_2/m_1$ |
|-----|-------------------|----------------------------------|----------------|----------------|-----------------------------|
| 1   | 5.165             | 2.0212                           | 69.27          | 30.73          | 0.3522                      |
| 2   | 7.564             | 2.0069                           | 68.78          | 31.22          | 0.3603                      |
| 3   | 4.666             | 1.1821                           | 40.52          | 59.48          | 1.1653                      |
| 4   | 5.769             | 1.1768                           | 40.33          | 59.67          | 1.1745                      |
| 5   | 5.530             | 1.1747                           | 40.26          | 59.74          | 1.1780                      |
| 6   | 3.746             | 1.1530                           | 39.52          | 60.48          | 1.1289                      |
| 7   | 6.132             | 1.0594                           | 36.31          | 63.69          | 1.3923                      |
| 8   | 6.199             | 1.0866                           | 37.20          | 62.80          | 1.3401                      |
| 9   | 4.014             | 0.6705                           | 22.98          | 77.02          | 2.6602                      |
| 10  | 3.041             | 0.6817                           | 23.37          | 76.63          | 2.6034                      |
| 11  | 4.546             | 0.4604                           | 15.78          | 84.22          | 4.2376                      |
| 12  | 5.574             | 0.4934                           | 16.91          | 83.09          | 3.9002                      |

TABLE 5  
Monomer Feed Composition: Copolymerization of  
Styrene and *p*-Divinylbenzene at 80°

| No. | Monomer feed, g |               |           | Wt.-%<br>styrene | Wt.-%<br><i>p</i> -DVB | Mole-%<br>styrene | Conversion,<br>% |
|-----|-----------------|---------------|-----------|------------------|------------------------|-------------------|------------------|
|     | Styrene         | <i>p</i> -DVB | $M_1/M_2$ |                  |                        |                   |                  |
| 1/2 | 0.6707          | 0.1804        | 4.6836    | 78.80            | 21.20                  | 82.41             | 0.55             |
| 3/4 | 0.6022          | 0.2365        | 3.2074    | 71.80            | 28.20                  | 76.23             | 0.94             |
| 5   | 0.2184          | 0.2646        | 1.0397    | 45.21            | 54.79                  | 50.97             | 1.72             |
| 6/7 | 0.2286          | 0.3166        | 0.9097    | 41.92            | 58.08                  | 47.63             | 1.05             |
| 8/9 | 0.4293          | 0.5065        | 0.6200    | 32.98            | 67.02                  | 38.27             | 2.08             |
| 10  | 0.1984          | 0.7786        | 0.3210    | 20.31            | 79.69                  | 24.30             | 1.78             |

The data for  $r_1$  and  $r_2 - m$  now available cover a substantial range of values. This is greater than is usually encountered in such studies and suggests that an additional understanding of this complicated copolymerization system is now possible. The changes in experimental conditions which are related to the differences in values are significant. Previous values ( $r_1 = 0.59$ ,  $r_2 - m = 0.57$ ) were obtained using a *t*-butylhydroperoxide catalyst at 100°C and a direct counting technique. We attribute the differences between the former values and present values partly to this use of a different

TABLE 6  
Copolymer Composition: Copolymerization of Styrene and  
*p*-Divinylbenzene at 80°; Ionization-Chamber Assay

| No. | Sample<br>wt., mg | Specific<br>charge,<br>mv/mg/sec | Wt.-%<br>$m_1$ | Wt.-%<br>$m_2$ | Molar<br>ratio<br>$m_2/m_1$ |
|-----|-------------------|----------------------------------|----------------|----------------|-----------------------------|
| 1   | 1.107             | 1.4846                           | 49.64          | 50.36          | 0.8053                      |
| 2   | 1.182             | 1.4763                           | 49.56          | 50.54          | 0.8113                      |
| 3   | 2.243             | 1.2273                           | 41.12          | 58.88          | 1.1365                      |
| 4   | 3.258             | 1.2859                           | 43.08          | 56.92          | 1.0488                      |
| 5   | 0.666             | 0.4328                           | 14.50          | 85.50          | 4.6823                      |
| 6   | 1.206             | 0.3881                           | 13.01          | 86.99          | 5.3090                      |
| 7   | 4.738             | 0.4228                           | 14.16          | 85.84          | 4.8110                      |
| 8   | 3.246             | 0.3452                           | 11.56          | 88.44          | 6.0739                      |
| 9   | 9.423             | 0.3436                           | 11.51          | 88.49          | 6.1050                      |
| 10  | 2.367             | 0.1880                           | 6.30           | 93.70          | 11.8049                     |

temperature and catalyst but, since this is probably not an entirely sufficient explanation, partly also to inherent limitations in the precision of the direct counting assay techniques.

The unusual feature of the new data for the meta-isomer copolymerization is that the values obtained at different conversion levels are different. The values are 0.605/0.88 at 1.8 to 3.7% (only one value over 2.2%) conversion and 1.27/1.08 at 2.7 to 7.5% conversion. It is to be noted that the values show a reversal of the relative magnitude of the two values. At low conversions  $r_1$  is lower than  $r_2$ ; at high conversions  $r_2$  is lower than  $r_1$ . This is consistent with an increased participation of the second of the divinyl units in the high-conversion copolymer. As the second vinyl unit becomes involved, the copolymerization system includes substantial contributions from a styrene/alkylstyrene copolymerization. Superposition of this on the styrene/meta divinylstyrene copolymerization results in a complication of the kinetics, presumably in the direction of a typical three-component system involving styrene, a vinylstyrene, and an alkylstyrene. The necessary data for comparisons with such three-component copolymerization systems, although readily obtainable by known techniques, are not available. The rather significant difference indicates, however, as we have suggested previously, that involvement of the second vinyl group is a significant factor in evaluating these data.

The change in copolymerization kinetics with change in catalyst and temperature deserves comment. The difference is significant enough to further substantiate the conclusion that the nature of the primary valence structure of polymers thus obtained will differ. This will, as noted in our previous studies, have a direct relation on such properties as sulfonation kinetics and swelling behavior of the cross-linked structures.

The para-divinylbenzene data (Tables 5 and 6, Figs. 6 and 7) give values of  $r_1 = 0.77$ ,  $r_2 - p = 2.08$  from the Fineman-Ross plot. These values differ from those previously reported (2) (0.15/0.5). The previous values were selected from an intersect plot with three intersects by disregarding the high-divinyl-content copolymer data. The present data (lower temperature, lower conversion, different catalyst) also do not show a clearly defined intersect. The stated values (0.77 and 2.08) were read from the least-squares analysis of the data on a Fineman-Ross plot. The fact that the  $r_1 r_2$  product is greater than 1.0 can be rationalized in terms of block-polymeriza-

tion tendencies. This would indicate an even greater clustering of the para cross-linkages than has been previously postulated on the basis of the selected values of  $r_1$  and  $r_2$ . Again, this is a factor related to copolymer characteristics.

We (11) also wish to record at this time the results of calculations of the  $r_1$  and  $r_2$  values for meta- and para-divinylbenzene using Hückel MO parameters (12) and the equations previously developed (13,14). The prediction of reactivity ratios from the calculated values  $\Delta E_{rs}$  was made using the correlation shown by Higasi et al. (15). The plotted data show no difference between styrene and *m*-divinylbenzene ( $r_1 \cong 1$ ,  $r_2 - m \cong 1$ ) and little apparent difference between styrene and *p*-divinylbenzene ( $r_1 = 0.75$ ;  $r_2 - p = 1.5$ ). It appears that these calculations, which are good only to a factor of 2 or 3, are not too useful even for prediction of the more reactive monomer of the pair.

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### Zusammenfassung

Reaktivitätsverhältnisse bei der Kopolymerisation von Styrol ( $r_1$ ), meta-Divinylbenzol ( $r_2 - m$ ) und para-Divinylbenzol ( $r_2 - p$ ) wurden bei verschiedenen Reaktionsbedingungen unter Benutzung verschiedener radioaktiver Methoden nachgearbeitet. Die Kopolymeren wurden bei zwei verschiedenen Umsetzungsgraden dargestellt [0.55–3.7% und 2.7–7.5% bei 80° (anstelle von 100°)] mit Benzoylperoxid als Initiator (anstelle von *t*-Butylhydroperoxid). Die für andere Kopolymerisationen entwickelte Methode, die aus einer Ionisationskammer und einem vibrierenden Zungenelektrometer zur radioaktiven Erfassung besteht wurde anstatt einer direkt arbeitenden Zählmethode benutzt welche früher bei den Styrol-Divinylbenzolsystemen angewandt wurde. Die neuen Werte sind  $r_1 = 0.605/r_2 - m = 0.88$ ;  $r_1 = 0.77/r_2 - p = 2.08$  bei einer Umsetzung von 0.55 bis 3.7% und  $r_1 = 1.27$ ;  $r_2 - m = 1.08$  bei 2.7–7.5% Umsetzung. Diese Werte stimmen nicht sehr gut mit den früheren Werten überein, teilweise auf Grund der Unterschiede in den Polymerisationsbedingungen (Temperatur, Prozent Umsatz, Initiator) und teils auf Grund der verbesserten analytischen Genauigkeit. In diesem Falle wurden die hohen DVB Werte (80%) im para-Kopolymeren nicht als ungültig angesehen und daher nicht (wie früher) bei der Auswahl der  $r_2 - p$  Werte weggelassen. Die neuen Werte zeigen jedoch dieselbe Art von alternierender Tendenz und sind ebenfalls in Übereinstimmung mit auf Hückel'schen MO-Berechnungen basierten Näherungen von  $r_1 = r_2 - m = 1$  und  $r_1 = 0.75/75$   $r_2 - p = 1.5$ .

### Résumé

Détermination nouvelle des rapports de réactivité de la copolymérisation du styrène ( $r_1$ ), du meta-divinylbenzène ( $r_2 - m$ ) et du para-divinylbenzène ( $r_2 - p$ ) dans des conditions de réaction différentes, avec des techniques nouvelles d'essai radioactif. On a préparé les copolymères à deux niveaux de conversion (0.55–3.7% et 2.7–7.5% et à 80° plutot qu'à 100°) avec le peroxyde de benzoyle (au lieu de *t*-butyl hydroperoxyde) comme initiateur. La technique d'essai de radioactivité de chambre de ionisation-électromètre vibrant à anche, développée pour d'autres études de copolymérisation a été utilisée au lieu de la technique du compte direct, employée précédemment pour les systèmes styrène/divinylbenzene. Les valeurs nouvelles sont  $r_1 = 0.605/r_2 - m = 0.88$ ;  $r_1 = 0.77/r_2 - p = 2.08$  à 0.55–3.7% de conversion et  $r_1 = 1.27$ ;  $r_2 - m = 1.08$  à 2.7–7.5% de conversion. Elles ne sont pas en bon accord avec les valeurs précédentes partiellement en raison de la différence dans les conditions de copolymérisation (température, pourcentage de conversion, initiateur), et grâce à la précision analy-

tique améliorée. On n'assume pas aussi que les données du copolymère para, élevées en DVB (80%), sont pas valides et ne sont pas omises (comme elles étaient précédemment) de la sélection des valeurs de  $r_2 - p$ . Cependant les nouvelles données montrent le même type des tendances alternantes. Elles sont aussi en accord avec les valeurs prévues, basées sur les calculs de Huckel pour MO de  $r_1 \cong r_2 - m \cong 1$  et  $r_1 = 0.75/75r_2 - p = 1.5$ .

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