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Monomer Reactivity Ratios from High Conversion Copolymerization of Styrene with meta- and with para-Divinylbenzene

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SUMMARY

The copolymerization reactivity ratios for styrene/m- and styrene/p-divinylbenzene have been determined at high conversions (<35%) using the integrated form of the copolymerization equation. Values of $r_1(s) = 1.11$, $r_2(m) = 1.00$; and $r_1(s) = 0.20$, $r_2(p) = 1.00$ were obtained. These values indicate the same relative behavior but are quantitatively different from the differential data. The data confirm that the para isomer is incorporated more rapidly into the growing polymer chain than is the meta isomer.

INTRODUCTION

The availability of the Fortran II program [1] for the solution of the integrated form [2] of the copolymerization equation makes studies [3, 4] of this type much more readily accomplishable. We have, therefore, extended our studies of the differential copolymerization behavior of the styrene(s)/meta- and styrene/para-divinylbenzene (DVB) stystems to such integral analyses with the objective of possibly resolving some of the uncertainties presented by the data for the differential analyses. The lack of intersect in the s/p-DVB plots is, e.g., particularly in need of clarification. The integrated form of the equation permits use of the copolymerization data for high conversion copolymers because it takes into account the drift in monomer feed and copolymer composition. This avoids errors encountered in the "low-conversion" data, required for the differential studies, such as those arising from low molecular weight species formed by termination by side reactions and impurities and from the handling of small quantities of copolymer. Both of these are problems of probable significance in the S/DVB systems and we are interested in their evaluation through this alternative approach to the reactivity ratios. The results of our study are recorded herewith.

EXPERIMENTAL

Materials

Commercial m-divinylbenzene (stabilized by 1000 ppm of inhibitor) of about 90% purity was supplied by Shell Chemical Company, New York. The commerical monomer was fractionated twice by preparative gas chromatography [5]. Analysis of the purified sample (Perkin-Elmer 154D gas chromatograph with thermal conductivity detector) showed the substance to be 99.8+% pure. p-Divinylbenzene was synthesized by the decarboxylation of p-phenylene-β,β-diacrylic acid [6] and fractionated by gas chromatography. The purified sample analyzed to 99.9+% purity. Styrene-β-C^{14} (stabilized by picric acid) of specific activity 0.13 mC/mmole (Tracer Lab Inc.) was diluted with pure distilled styrene in a nitrogen atmosphere to specific activity of 1 mμC/mmole. All monomers were stored below 5°C in the presence of inhibitor and distilled under vacuum prior to use. Benzoyl peroxide (Fisher Scientific Co.) was recrystallized from chloroform-methanol mixtures and dried.

Polymerization Procedure

The weighed Pyrex reaction cell was charged with an appropriate quantity of divinylbenzene in nitrogen atmosphere and reweighed. Radioactive styrene was distilled into the reaction cell employing the vacuum line techniques described earlier [7]. Monomer mixtures of weight ratios ranging from 2.5 to 0.3 were prepared. The total weight of the monomer mixture in each case was nearly 1 g. A solution of benzoyl peroxide in benzene (0.5 ml), followed by benzene (0.5 to 1.0 ml), was added to the reaction mixture under nitrogen. The weight of benzoyl peroxide was 0.1% by weight of the monomer mixture. The reaction mixture was chilled in liquid nitrogen, degassed in vacuum, and remelted. The freezing and thawing was repeated 3 or 4 times before the cell was sealed.

The polymerizations were carried out in a water thermostat maintained at 75 ± 0.1°C for 30 to 200 min (to conversion ranges of 2–35%). The polymerizations were stopped by freezing the cells in Dry Ice–acetone mixtures at appropriate times. The polymers were recovered by precipitation by methanol. The chilled reaction cell was carefully broken, and the contents of the cell were treated with 0.5 to 1 ml of benzene containing a small amount of inhibitor and mixed with a spatula to form a uniform slurry which was then transferred to a weighed centrifuge tube. The cell was washed 3 or 4 times with benzene and the contents were again transferred to the centrifuge tube. Final washing of the cell was done with 1 ml of methanol to make sure that no turbidity appears in the methanol washing, indicating the complete removal of polymer in earlier washings. About 5–10 ml of methanol was added and the contents were again thoroughly stirred to complete mixing and precipitation. The tube was centrifuged for 20 min at 1500 rpm. The clear supernatent liquid was carefully decanted to avoid any loss of the polymer. The reprecipitation of the polymer (dissolving in benzene and precipitation by methanol) was carried out 3 or 4 times to ensure the complete removal of the adhering monomers and initiator. In the case of less soluble, cross-linked materials, the polymers were swollen well in benzene before treatment with methanol. After complete purification, the polymer was again dissolved in a small quantity of benzene (2–5 ml) and the tube was gently rotated over a bed of Dry Ice to freeze the polymer solution uniformly on the sides of the tube. The centrifuge tube was then immediately transferred to a vacuum dessicator and evacuated for 3 to 4 hr. The centrifuge tube was then covered with an aluminum foil with holes in it and evacuated at 0.1 to 1 mm and 45–55°C for more than 48 hr and until constant weight was obtained.

Radioactivity Assay

The copolymers were analyzed for styrene-β-C^{14} content using the procedure described earlier [8, 9]. About 2–10 mg of the copolymer sample was accurately weighed to a microgram in a procelain combustion boat and placed in a quartz combustion train set up following the standard procedure [10]. Medical oxygen containing 5% of carbon dioxide was used for combustion at the rate of 15 ml/min. The polymer was ignited at a controlled rate (15–20 min) and the combustion products were carried by the oxygen gas through the furnace (700°C) to an evacuated, spherical ionization chamber of about 500 ml capacity. The polymer was completely burnt to carbon dioxide. The radioactive content of the carbon dioxide was assayed using a vibrating reed electrometer with a recorder (Cary Instruments, Applied Physics Corp. Model 31) by determining the time required to build up a given charge. An average of 5 to 6 charge rate readings on the recorder was taken. Duplicate analyses checked with an accuracy of 0.06–1.4%. A background was run with the oxygen gas and the specific charge rate of the sample with that of the standard.

Computer Program Operations

The Fortran II computer program for the integrated form of the copolymerization equation (a slightly modified version of the original Mayo and Lewis [2] integrated equation) as described by Montgomery and Fry [1] was used for treatment of the conversion and composition data to obtain r_1 and r_2 values. The input data (Tables 1 and 2) consist of the initial (feed) weight fraction of each monomer, the fractional conversion, the weight fraction of each monomer in the copolymer (from radioactivity assay data given in Tables 1 and 2), and the molecular weight of each monomer for any two experiments. For reasons given previously the equivalent weight of the divinyl monomer is taken as half the molecular weight in calculating the monomer feed weight fraction. "The program operates by calculating r_2 in terms of the arbitrary P for each of the data points, then incrementing P in such a manner that the two r_2 values converge to the unique value common to both points. The r_2, with the corresponding P is then used to calculate r_1" [1]. P is defined as equal to $(1 - r_1)/(1 - r_2)$. An IBM 1620 data processing system and IBM 1622 card read punch were used. The read-out is summarized in Tables 3 and 4.

Analysis of Experimental Deviations

The radioactivity assay shows the least experimental variation in our data (±1% in duplicate analysis). Deliberate alterations of ±10% in the conversion data (Tables 3 and 4) as used in computer input calculations give an average variation of ±0.8% in S/m-DVB and ±2% in S/p-DVB except for one set of data for which the deviation is 27.5%. Deviations caused by benzoyl or phenyl end groups on the copolymer analysis, even for the lowest conversion

Table 1. Monomer Feed Composition, Copolymer Composition, and Conversion Data for the Styrene (M_1/m-Divinylbenzene (M_2) Copolymerization

Expt No.	Monomer feed, (g) M_1	Monomer feed, (g) M_2	Weight fraction in feed M_1[a]	Weight fraction in feed M_2[b]	Copolymer composition[c] M_1	Copolymer composition[c] M_2	Conversion (%)	Specific change rate (× 10^2) (mV/sec/mg[d])	Wt % styrene
1	0.7006	0.2977	0.5406	0.4594	0.5086	0.4913	4.770	3.3715	50.86
2	0.5957	0.2729	0.5218	0.4781	0.5286	0.4713	18.24	3.5040	52.86
3	0.4920	0.4261	0.3660	0.6339	0.3755	0.6244	67.85	2.4895	37.55
4	0.6066	0.3924	0.4359	0.5640	0.4854	0.5146	24.47	3.2175	48.54
5	0.2991	0.8411	0.1509	0.8490	0.2236	0.7763	34.96	1.4825	22.36

[a] Equivalent weight fraction of styrene in the monomer feed from the relation M_1,g/(M_1,g + M_2,2g).

[b] Equivalent weight fraction of m-divinylbenzene in the monomer feed from the relation M_2,2g/(M_1,g + M_2,2g).

[c] Weight fraction of M_1 and M_2 in the copolymer.

[d] Specific charge rate for reference polystyrene, 6.6285 × 10^{-2} mV/sec/mg. Value is average for two determinations corrected for the background value (0.1167 mV/sec); av deviation, ±0.61%; max deviation, ±1.4%.

Table 2. Monomer Feed Composition, Copolymer Composition, and Conversion Data for the Styrene (M_1)/p-Divinylbenzene (M_2) Copolymerization

Expt No.	Monomer feed (g) M_1	Monomer feed (g) M_2	Weight fraction in feed M_1[a]	Weight fraction in feed M_2[b]	Copolymer composition[c] M_1	Copolymer composition[c] M_2	Conversion (%)	Specific change rate (× 10^2) (mV/sec/mg[d])	Wt % styrene
6	0.7313	0.3160	0.5363	0.4336	0.3897	0.6102	1.928	2.5835	38.97
7	0.6306	0.2760	0.5332	0.4668	0.4072	0.5927	14.95	2.6995	40.72
8	0.3948	0.4939	0.2855	0.7145	0.2290	0.7770	14.89	1.4775	22.29
9	0.4002	0.6669	0.2308	0.7692	0.1833	0.8166	9.042	1.2155	18.33
10	0.3810	0.8215	0.1882	0.8117	0.2475	0.7524	19.37	1.6410	24.75

[a] Equivalent weight fraction of styrene in the monomer feed from the relation M_1,g/(M_1,g + M_2,2g).

[b] Equivalent weight fraction of p-divinylbenzene in the monomer feed from the relation M_2,2g/(M_1,g + M_2,2g).

[c] Weight fraction of M_1 and M_2 in the copolymer.

[d] Specific change rate for polystyrene 6.6285 × 10^{-2} mV/sec/mg. The value given is the average of two values, corrected for the background value (0.1167 mV/sec); av deviation, ±0.82%; max deviation ±1.19%.

Table 3. Monomer Reactivity Ratios (r_1 and r_2) for the Styrene/m-Divinylbenzene Copolymerization

Pairs[a,b]	Av conversion (%)	r_1[c]	r_2[d]
1(4.7), 3(6.7)	5.7	0.95	1.00
1(4.7), 2(18.2)	11.4	0.92	1.00
3(6.7), 2(18.2)	12.4	1.08	1.00
1(4.7), 4(24.4)	14.5	1.16	1.00
3(6.7), 4(24.4)	15.5	1.31	1.00
2(18.2), 4(24.4)	21.3	1.29	1.00

[a] Pairs of data points used, identified as expt numbers in Table 1 with the conversion in parenthesis.

[b] Variation of these values by ±10% gave r_1 values (top to bottom) of 0.912, 0.920, 1.077, 1.157, 1.314, 1.292, and r_2 values of 1.00.

[c] Average, r_1 = 1.11.

[d] Average, r_2 = 1.00.

Table 4. Monomer Reactivity Ratios (r_1 and r_2) for the Styrene/p-Divinylbenzene Copolymerization

Pairs[a,b]	Av conversion (%)	r_1[c]	r_2[d]
6(1.93), 9(9.04)	5.48	0.15	1.00
6(1.93), 8(14.89)	8.41	0.25	1.01
6(1.93), 7(14.95)	8.44	0.25	1.01
7(14.95), 9(9.04)	11.99	0.18	1.00
7(14.95), 8(14.89)	14.92	0.21	1.00

[a] Pairs of data points used, identified as expt numbers in Table 2 with the conversion in parenthesis.

[b] Variation of these values by ±10% gave r_1 values (top to bottom) of 0.149, 0.182, 0.268, 0.178, 0.209, and r_2 values of 1.00

[c] Average, r_1 = 0.20.

[d] Average, r_2 = 1.00.

copolymer, is 1.0% and is much less for higher conversion copolymers.

Results and Discussion

Values of $r_1(S) = 1.11$ and $r_2(m\text{-DVD}) = 1.00$ were obtained for the S/m-DVB copolymerization (Tables 1 and 3) from data for the 4–25% conversion range. We have previously observed values of $r_1 = 0.605$, $r_2 = 0.88$, and $r_1 = 1.27$, $r_2 = 1.08$ from differential analyses at 0.55–3.72% and 2.7–5% conversion levels, respectively [3]. The trend toward higher r_1 values (up to 3.92) at higher conversions is confirmed in integral data (Table 5) for the copolymerizations up to 35% conversion and with less than 1/1 ratio of S/m-DVB. It thus appears, subject to clarification of the high conversion discrepancies, that the S/m-DVB system involves copolymerization of two monomers of approximately equivalent reactivity, neither radical showing a great preference for either its own or the comonomer. Deviation from this equivalence is in the direction of enhanced reactivity of styrene radical towards styrene monomer and this deviation is enhanced at high conversions.

For the S/p-DVB system (Tables 2 and 4), values of $r_1(S) = 0.20$ and $r_2(p\text{-DVB}) = 1.00$ are obtained from the integral analysis at conversion levels in the 2–15% range (Table 4). The value of r_1 again, as with the meta isomer, is much higher (1.67–1.76) for copolymers prepared at higher (15-19%) conversions and with less than 1/1 S/p-DVB monomer ratios (Table 5). These values are to be compared with the differential values previously observed: $r_1 = 0.77$, $r_2 = 1.46$ (0.55–3.7% conversion) [4] and

Table 5. Monomer Reactivity Ratios (r_1 and r_2) for the Styrene/m- and p-Divinylbenzene Copolymerization

Pairs[a]	Av conversion (%)	r_1	r_2
1(4.7), 5(34.9)	19.8	3.77	1.00
3(6.7), 5(34.9)	20.8	3.92	1.00
2(18.2), 5(34.9)	26.5	3.90	1.00
8(14.89), 10(19.37)	17.13	1.67	0.99
7(14.95), 10(19.37)	17.16	1.76	0.99

[a] Pairs of data points used, identified as expt numbers in Tables 1 and 2 with the conversion in parenthesis.

r_1 = 0.77, r_2 = 2.08 (2–5.2% conversion) [3]. It is to be noted that the solutions of the differential equation were unsatisfactory, as seen in intersect plots [3, 4], in the absence of simplifying assumptions. It is, however, reasonably and consistently clear from all of the low conversion data that in the S/p-DVB system the two radicals are unlike in their behavior toward the two monomers. p-DVB is much the more reactive monomer to either radical. The system differs from that of S/m-DVB in showing an inversion in the reactivity ratios for the high conversion copolymers at high DVB content. It is this factor that probably leads to the erratic results in the differential analyses. If this hypothesis is accepted, it follows that the contrast in r_1 and r_2 is much greater at low conversion–low DVB content than had previously been apparent; i.e., the 0.2/1.0 values are most realistic. This indicates that the relative bunching of cross-linkages is of marked significance.

The enchanced r_1 values obtained at higher conversions and with the low S/DVB monomer ratios are attributable to diffusion problems. At the higher levels a relatively minor involvement of the second vinyl group leads to cross-linking and this in turn inhibits ready diffusion of the more bulky divinyl monomer to the growing radical site. Comparison of the magnitude of the effect in the m-DVB (nearly fourfold) and p-DVB (over eightfold) shows that the p-DVB system shows both greater enhancement of r_1 and enhancement at lower conversion levels; i.e., 19% as opposed to 35%. This is consistent with our observation that the S/p-DVB system cross-links (gels) at lower conversion and shorter times than does the S/m-DVB system and swells less.

It is to be noted that the lack of sensitivity in the r_1 and r_2 values to arbitrary alterations in the conversion data is because the copolymer composition does not vary greatly at high conversions.

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