Monomer Reactivity Ratios for the Copolymerization of p-lsopropylstyrene with Styrene and Methyl Methacrylate

Richard H. Wiley[a]; Jung-Il Jin[a]

[a] Department of Chemistry, Hunter College of the City University of New York, New York, New York

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RICHARD H. WILEY and JUNG-IL JIN

Department of Chemistry
Hunter College of the City University of New York
New York, New York

SUMMARY

The monomer reactivity ratios for the copolymerizations of p-isopropylstyrene with styrene and with methyl methacrylate have been determined by the ionization chamber-vibrating reed electrometer radio-activity assay technique. The values from the differential form of the copolymerization equation are r_1 (styrene) = 1.22, r_2 (p-isopropylstyrene) = 0.89, and r_1 (methyl methacrylate) = 0.44, r_2 (p-isopropylstyrene) = 0.39. The values from the integrated form of the equation are r_1 (styrene) = 1.37 and r_2 = 0.99. These values indicate that, in the copolymerization of p-divinylbenzene (p-DVB) with styrene, the p-isopropylstyrene-like unit, formed from having the first vinyl group of p-DVB reacted, takes part in subsequent propagation reactions with styrene less readily than either styrene or p-DVB.

INTRODUCTION

The copolymerization characteristics for m- and p-divinylbenzenes have been studied in some detail [1, 2]. The styrene and m-DVB copolymerization system gives reasonable and well-defined monomer reactivity ratios, but the styrene-p-DVB system gives neither well-defined solutions of the

copolymer composition equation nor satisfactorily reproducible values. The same phenomena were observed in the copolymerizations of methyl methacrylate with m-DVB and with p-DVB. In an attempt to clarify the situation presented by the p-DVB copolymerization data, the results of the copolymerization of p-isopropylstyrene with styrene and with methyl methacrylate are presented.

Data for the p-isopropylstyrene are of interest because this monomer presents a structural model for the cross-linking polymerization of the pendant vinyl groups of p-DVB monomer units incorporated in the polymer chain by copolymerization of the first of its vinyl groups.

EXPERIMENTAL

Monomers

Styrene-β-^{14}C, supplied by Tracerlab, Inc., with a specific activity of 0.17 mCi/mmole was diluted with 240 volumes of freshly distilled unlabeled styrene (Baker Chemical Co.), n_D^{20} 1.5464, and was stored under nitrogen at $-10°C$ with 2,6-di-tertiary-butyl-p-cresol (Eastman Organic Chemicals) as stabilizer until used.

Methyl-^{14}C methacrylate was prepared and supplied by Tracerlab, Inc. with a specific activity of 0.34 mCi/mmole. The sample contained 239.9 mg (0.314 ml) with a total activity of 1.0 mCi and was stabilized with hydroquinone. This was diluted with 500 volumes of freshly distilled methyl methacrylate (Eastman Organic Chemicals), n_D^{20} 1.4135, and was stored under the same conditions mentioned above.

p-Isopropylstyrene was synthesized by decarboxylation of p-isopropylcinnamic acid prepared from p-isopropylbenzaldehyde and malonic acid via the Doebner condensation reaction as previously described [3]. The yield of p-isopropylcinnamic acid from 62.44 g (0.6 mole) of malonic acid and 74.1 g (0.5 mole) of p-isopropylbenzaldehyde was 49.3 g (0.26 mole, 52%), mp 157.5-159°C. The yield of p-isopropylstyrene from 65 g (0.34 mole) of this acid was 45.2 g (0.31 mole, 91%), n_D^{20} 1.5290, bp 85°C/12 mm (reported [4] bp 45°C/1.3 mm, n_D^{24} 1.5190).

Initiator

Dibenzoyl peroxide (Fisher Scientific Co.) was purified by methanol precipitation from concentrated chloroform solution and vacuum dried.

Table 1. Copolymerization of Styrene and p-Isopropylstyrene

Expt. no.	Monomer feed, g		Monomer molar ratio, M_1/M_2	Conversion, wt. %	Specific charge rate[a]	Molar ratios in copolymer[b], m_2/m_1
	Styrene	p-iPS				
1	1.92604	0.78410	3.4488	3.305	0.06043	0.2393
2	0.97545	0.40772	3.3591	5.739	0.05964	0.2518
3	0.67733	0.64609	1.4719	5.374	0.04441	0.5823
4	0.79158	1.92366	0.57777	4.944	0.02636	1.4685
5	0.26807	1.07953	0.34865	2.081	0.01779	2.5193

[a] (Charge/time−background)/weight in mV/sec/mg. Average of two determinations.
[b] Control on labeled polystyrene, 0.080725 mV/sec/mg.

Table 2. Copolymerization of Methyl Methacrylate and p-Isopropylstyrene

Expt. no.	Monomer feed, g		Molar ratio, M_1/M_2	Conversion, wt. %	Specific charge rate [b]	Molar ratios in copolymer [c], m_2/m_1
	MMA	p-iPS				
1	1.98845	0.78977	3.6773	3.506	1.85165	0.4483
2 [a]	1.98845	0.78977	3.6773	3.347	1.85184	0.4483
3	0.72210	0.64345	1.6391	2.600	1.46065	0.7516
4	0.60373	0.70438	1.2518	2.987	1.34817	0.8715
5	0.45655	0.93177	0.71564	3.285	1.12574	1.1789
6	0.31075	0.95468	0.47541	2.971	0.95278	1.5172

[a] One monomer mixture was divided into two portions for Expt. 1 and Expt. 2.
[b] (Charge/time−background)/weight. Average of two determinations.
[c] Control on labeled polymethyl methacrylate, 3.06415 mV/sec/mg.

Copolymerization and Analysis of Copolymer

The monomers for copolymerizations were distilled under vacuum at room temperature from stock solutions into the polymerization cells just prior to use by vacuum line techniques as described earlier [5]. The reaction cells were weighed before and after the addition of each monomer under a nitrogen atmosphere. After the addition of benzoyl peroxide (0.1% by weight of monomers), the cells were degassed and sealed under vacuum. The copolymerizations were carried out at $70 \pm 0.1°C$ in water bath. The copolymerizations of styrene and p-isopropylstyrene pairs were stopped after 30-86 min to give the conversions given in Table 1. The methacrylate and p-isopropylstyrene copolymerizations were stopped after 56-62 min to give the yields given in Table 2. The polymerizations were stopped by freezing in a dry-ice acetone bath. The copolymers were thawed, quickly transferred to centrifuge tubes containing small amounts of inhibitor, and precipitated by adding sufficient amounts of methanol. The polymer remaining after decantation of the solvent and unreacted monomer mixture was redissolved in benzene and reprecipitated by methanol. This process was repeated three to five times to remove monomers prior to final drying. After vacuum drying, the polymer was analyzed by the ionization chamber-vibrating reed electrometer radio-activity assay technique [6] previously employed by us [5]. The analytical data are shown in Tables 1 and 2.

RESULTS AND DISCUSSION

The reactivity ratios for a binary copolymerization were obtained from monomer-feed data and copolymer compositions using the differential form of the copolymer composition equation [7]. The data for the copolymerizations of p-isopropylstyrene with styrene and with methyl methacrylate are given in Tables 1 and 2 and in Figs. 1-4. The least-squares analyses for the Fineman-Ross plots [8] give r_1 (styrene) = 1.22, r_2 (p-isopropylstyrene) = 0.89, and r_1 (methyl methacrylate) = 0.44, r_2 (p-isopropylstyrene) = 0.39. Although these values for r_1 (styrene) and r_2 are not in close accord with the values reported in earlier studies [9] (r_1 = 1.11, r_2 = 0.54), we believe that the differences arise from differences in the analytical procedures used. In other systems, notably for S/MMA, the radioactivity assay technique gives reliable results.

The Q and e values for p-isopropylstyrene calculated from the Alfrey-Price equations [10] using r_1 (MMA) = 0.44 and r_2 (p-iPS) = 0.39 values

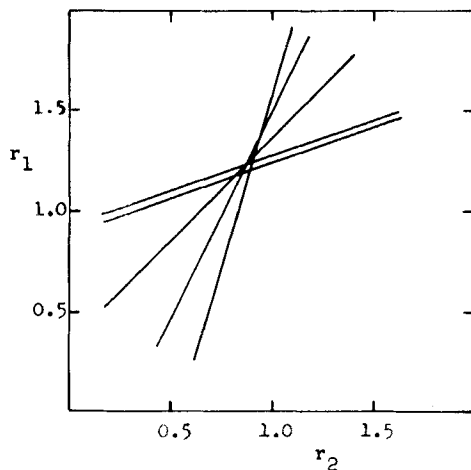**Fig. 1.** Intersect plot for the copolymerization of styrene (r_1 = 1.22) and p-isopropylstyrene (r_2 = 0.89). Benzoylperoxide initiator at 70°C.
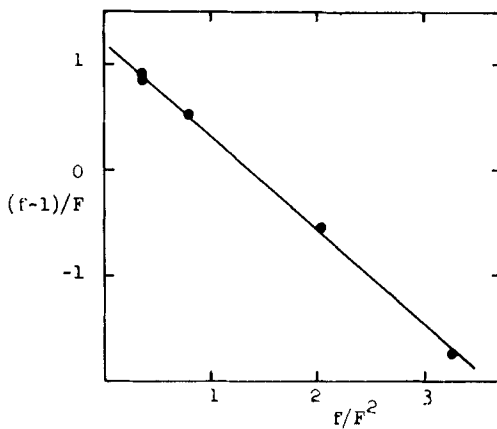

Fig. 2. Fineman-Ross plot for the copolymerization of styrene (r_1 = 1.22) and p-isopropylstyrene (r_2 = 0.89). Benzoylperoxide initiation at 70°C. Slope and intersect by least-squares regression analysis.
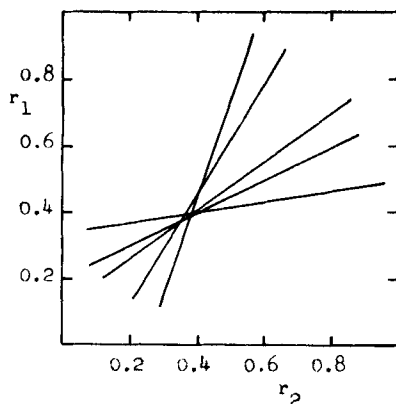
Fig. 3. Intersect plot for the copolymerization of methyl methacrylate (r_1 = 0.42) and p-isopropylstyrene (r_2 = 0.38). Benzoylperoxide initiator at 70°C.

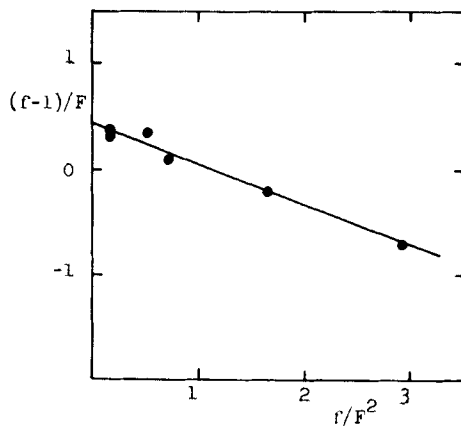**Fig. 4.** Fineman-Ross plot for the copolymerization of methyl methacrylate (r_1 = 0.44) and p-isopropylstyrene (r_2 = 0.39). Benzoylperoxide initiator at 70°C. Slope and intersect by least-squares regression analysis.

are $Q = 1.1$ and $e = -0.9$ on the basis of values of $Q = 1.0$ and $e = -0.8$ for styrene. These values are in the same range as those for p-methoxystyrene ($Q = 1.1$, $e = -1.2$) [11] and p-methylstyrene ($Q = 1.05$, $e = -0.9$) [11]. For the styrene-p-isopropylstyrene copolymerizations, the r_1 value is greater than the r_2 value, whereas the best chosen r_1 (styrene) value (0.77) is much less than the best chosen r_2 (p-DVB) value (2.08) for the copolymerization of styrene and p-DVB. This shows that p-isopropylstyrene is less active to the styrene radical than styrene. Styrene, in turn, is less active to this radical than p-DVB.

Using the computer program described by Montgomery and Fry [12], we have calculated the monomer reactivity ratios from the integrated form of the copolymer composition equation [13]. The monomer charge ratio, copolymer composition, and conversion data for all 20 combinations of pairs of experiments in Table 1 were used in the Fortran II program as input data. Values of $r_1 = 1.37$ and $r_2 = 0.99$ were obtained as averages of results for all 20 pairs. Of these, experiments 4 and 5 (used as the first members of the pairs) gave much higher values of r_1 (1.44-1.54) than those ($r_1 = 1.24$-1.29) from experiments 1, 2, and 3 (taken as first members of the pairs). Although these (numbers 4 and 5) are for the low styrene composition experiments, we have no basis for excluding them from the averages for this reason. It was noted by Montgomery and Fry [12] that the r_1 values they obtained for vinyl acetate-vinyl chloride reactivity ratios were higher than those from differential analysis.

The conclusion on the basis of these data is that cross-linking in the styrene-p-DVB system, which involves polymerization of a p-isopropylstyrene-like monomer unit, is somewhat less favorable than linear chain polymerization through either styrene- or p-DVB-derived terminal radicals. The iPS monomer type is somewhat the least reactive of the three structural monomer types—iPS, styrene, and p-DVB—toward the styrene radical. On the other hand, since the difference in r_1 and r_2 for the S/iPS system is not great, it may well be possible to describe the S/p-DVB system as a three-component copolymerization, as previously suggested [1].

ACKNOWLEDGMENTS

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