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Monomer Reactivity Ratios for the Copolymerization of Methyl Methacrylate with Pure Meta- and Pure Para-Divinylbenzene

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Monomer Reactivity Ratios for the Copolymerization of Methyl Methacrylate with Pure Meta- and Pure Para-Divinylbenzene

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SUMMARY

The monomer reactivity ratios for methyl methacrylate (MMA) with pure meta-divinylbenzene (m-DVB) and with pure para-divinylbenzene (p-DVB), determined with radioactivity assay techniques, are $r_1(\text{MMA}) = 0.41$, $r_2(\text{m-DVB}) = 0.61$ and $r_1(\text{MMA}) \simeq 0.62$, $r_2(\text{p-DVB}) \simeq 1.3$. The data for the MMA/m-DVB pair give a fairly precise solution of the copolymerization equation and are in accord with previously observed styrene (S)/methyl methacrylate values [8] ($r_1 = 0.52$, $r_2 = 0.41$). The data for the MMA/p-DVB pair, as was also observed for the S/p-DVB pair, do not give an entirely satisfactory solution for the equation but do indicate a substantial preference of both (p-DVB and MMA or S) radicals for the p-DVB monomer and thus confirm a postulated clustering of p-DVB units.

INTRODUCTION

The monomer reactivity ratio data for the styrene/m-divinylbenzene and styrene/p-divinylbenzene pairs have been studied in some detail [1]. The S/m-DVB data give reasonable solutions for the copolymerization equation, but the S/p-DVB data give neither reasonable solutions to the equation nor reproducible values. In the interests of providing further understanding of these phenomena we have undertaken a study of the copolymerization kinetics of methyl methacrylate with pure meta- and pure para-divinylbenzene and wish to record our observations herein.

RESULTS AND DISCUSSION

The data for the meta-divinylbenzene copolymerizations from Tables 1 and 2 are presented in intersect (Fig. 1) and Fineman-Ross (Fig. 2) plots [7]. The intersect is reasonably definitive and the points fit the linear plot reasonably well. The least-squares

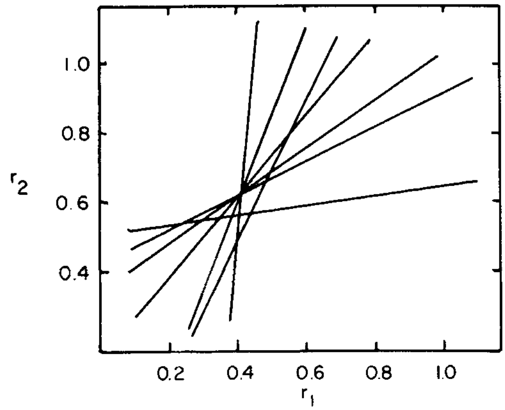

Fig. 1. Intersect plot for the copolymerization of methyl methacrylate ($r_1 = 0.41$) with m-divinylbenzene ($r_2 = 0.61$) at 70°C with benzoyl peroxide initiator. The data are for duplicate analyses on the copolymers in Tables 1 and 2.

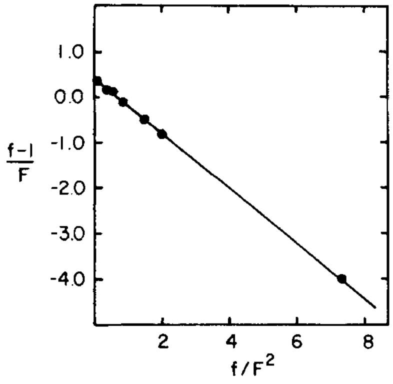

Fig. 2. Fineman-Ross plot for the copolymerization of methyl methacrylate ($r_1 = 0.41$) and m-divinylbenzene ($r_2 = 0.61$). The data are for duplicate analyses on the copolymers described in Tables 1 and 2, and the line is located by least-squares regression analysis.

Table 1. Monomer Feed Composition: Copolymerization of Methyl Methacrylate and m-Divinylbenzene

Expt. No.	Monomer feed, g Methyl methacrylate (M_1)	 m-DVB (M_2)	Molar ratio $M_1/2M_2$	Conversion %
1	0.3166	1.1105	0.1854	5.62
2	0.6947	0.8621	0.5239	6.52
3	0.8349	0.8055	0.6739	5.98
4	1.0375	0.6630	1.0173	5.47
5	1.2325	0.5242	1.5286	5.29
6	1.3177	0.4873	1.7581	4.22
7	1.7693	0.2003	5.7434	3.01

Table 2. Copolymer Composition: Copolymerization of Methyl Methacrylate and m-Divinylbenzene

Expt. No.	Specific charge rate, mV/sec/mg[a]	Wt. % m_1[b]	Wt. % m_2	Molar ratio m_2/m_1
1	0.5434	16.28	83.72	3.956
2	0.9986	29.92	70.08	1.801
3	1.1270	33.77	66.23	1.509
4	1.3421	40.21	59.79	1.144
5	1.6080	48.18	51.82	0.827
6	1.6788	50.30	49.70	0.760
7	2.3370	70.02	29.98	0.329

[a] (Charge/time-background)/weight. Background was 0.1420 mV/sec. Average of two determinations. Deviation: average, ± 0.6%; maximum, ±1.2%.

[b] Control on labeled poly(methyl methacrylate) 3.3377 mV/sec/mg.

analysis for the linear plot gives values of $r_1 = 0.41$ and $r_2 = 0.61$. The Q and e values calculated by the Alfrey-Price equations [9] with these data are $Q = 1.1$ and $e = -0.8$. These values are in the same range as those for p-methoxystyrene ($Q = 1.0$, $e = -1.0$), p-methylstyrene ($Q = 1.05$, $e = -0.9$), and m-methylstyrene ($Q = 0.95$, $e = -0.8$). The calculated r_1 and r_2 values for the copolymerization system of styrene/m-DVB using the Q and e values (1.1 and -0.8, respectively) for MMA/m-DVB are $r_1 = 0.90$ and $r_2 - m = 1.1$. These values are reasonably close to the values $r_1 = 1.27$ and $r_2 - m = 1.08$ reported earlier [1].

The data for the para-divinylbenzene copolymerizations from Tables 3 and 4 are presented in intersect (Fig. 3) and linear (Fig. 4) plots. The intersect plot does not give a satisfactory solution for the copolymerization equation, and deviation from the linear plot is great. The intersect plot resembles that for the S/p-DVB system. If all the experimental data given in the figures and tables are used, values of $r_1 = 0.10$ and $r_2 = 0.93$ are obtained by a least-squares

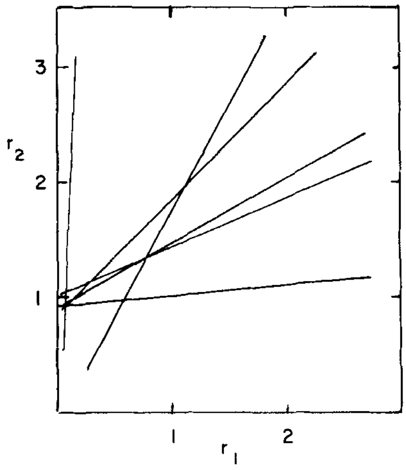

Fig. 3. Intersect plot for the copolymerization of methyl methacrylate ($r_1 = 0.62$) with p-divinylbenzene ($r_2 = 1.3$) at 70°C with benzoyl peroxide initiator. The data are for duplicate analyses on the copolymers in Tables 3 and 4.

Table 3. Monomer Feed Composition: Copolymerization of Methyl Methacrylate and p-Divinylbenzene

Expt. No.	Monomer feed, g Methyl methacrylate (M_1)	 p-DVB (M_2)	Molar ratio $M_1/2M_2$	Conversion %
1	1.1034	0.1489	4.8182	2.81
2	0.9553	0.4386	1.4161	2.77
3	0.7322	0.7384	0.6447	3.07
4	0.5120	0.8102	0.4109	2.85
5	0.4454	0.9954	0.2910	2.95
6	0.1451	1.2929	0.0729	1.04

Table 4. Copolymer Composition: Copolymerization of Methyl Methacrylate and p-Divinylbenzene

Expt. No.	Specific charge rate, mV/sec/mg[a]	Wt. % m_1	Wt. % m_2	Molar ratio m_2/m_1
1	1.5530	46.53	53.47	0.884
2	1.5218	45.59	54.41	0.918
3	0.8200	24.57	75.43	2.361
4	0.6420	19.24	80.76	3.229
5	0.4806	14.40	85.60	4.572
6	0.1791	5.36	94.64	13.570

[a] (Charge/time-background)/weight. Background was 0.1420 mV/sec. Average of two determinations. Deviation: average, ±0.72%; maximum, ±1.56%.

[b] Control on labeled poly(methyl methacrylate) 3.3377 mV/sec/mg.

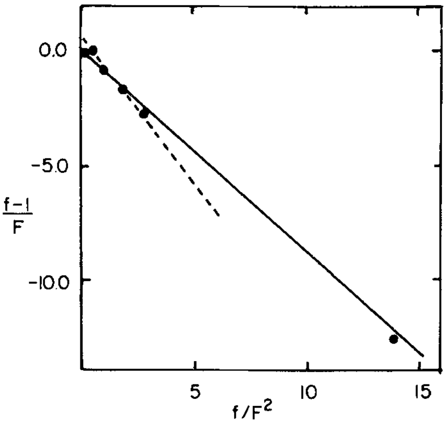

Fig. 4. Finemann-Ross plot for the copolymerization of methyl methacrylate ($r_1 = 0.62$) and p-divinylbenzene ($r_2 = 1.3$). The data are for duplicate analyses on the copolymers described in Tables 3 and 4 and the lines are located by least-squares regression analysis. The solid line is calculated from all points, the dashed line without the extreme points.

analysis of the linear plot (Fig. 4, solid line). This includes data for two copolymerizations, those with 9.4 and 87.3 mole % p-DVB, which deviate greatly from the data for the other four runs. If these two are omitted from the analysis of the data, values of $r_1 = 0.62$ and $r_2 = 1.30$ are obtained from the linear plot (Fig. 4, dashed line). These values are in fair accord with those from the S/p-DVB copolymerizations ($r_1 = 0.77, r_2 = 2.08$).

We have commented previously on the significance of the p-divinylbenzene reactivity ratios. Both lack of precise intersects and wide variations in observed data depending on experimental conditions have been observed [1, 10]. Because the values of r_1 are usually, no matter how the data are treated, rather low (about 0.8) and the values for r_2 usually rather high (about 1.5), it seems safe to postulate that para-divinylbenzene monomer is preferentially reactive with its own (p-DVB) and the other (S or MMA) radicals. Furthermore, the fact that the r_1, r_2 product is over 1.0 indicates block formation. These factors are interpreted to mean there is more clustering of the divinyl units in the para- than in the meta-DVB copolymers. This is consistent with various types of previously reported [11-13] physical data characterizing the two types of cross-linked polymers and recently reported [14] mass spectrometric analyses.

EXPERIMENTAL

Monomers

Methyl ^{14}C-methacrylate was supplied by Tracerlab, Inc. with a specific activity of 0.34 mCi/mm. This sample was diluted with 450 volumes of freshly distilled unlabeled methyl methacrylate (Eastman Organic Chemicals), N_D^{28} 1.4100, and was stored under nitrogen at −10°C with a 2, 6-di-t-butyl-p-cresol (Eastman Organic Chemicals) as stabilizer until used.

Meta-divinylbenzene (supplied by Centre de Recherches du Groupe Petrofina, Brussels, with purity of 95+%) and para-divinylbenzene (supplied by Cosden Chemical Co. with purity of about 90%) were purified and characterized by the methods reported earlier [2, 3]. The monomers as used were 99.5+% pure by gas chromatographic analysis using Perkin-Elmer R column and flame ionization detector.

Initiator

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

Copolymerization

The monomer mixtures were prepared by vacuum line techniques as described previously [4]. The copolymerizations were carried out at 70 ± 0.1°C in a water bath with 0.1 wt.% dibenzoyl peroxide as initiator. The copolymerizations of methyl methacrylate and meta-divinylbenzene pairs were stopped after 30 to 100 min to give 3-6.5% of copolymer. The methyl methacrylate and para-divinylbenzene copolymerizations were stopped at or before gelation to give copolymer yields of 1 to 3% (30-55 min). The copolymers were isolated as follows. At the end of a copolymerization, the reaction tube was immersed in a Dry Ice-acetone bath to be frozen. After the mixture had been frozen, the tube was removed from the Dry Ice-acetone mixture and 0.5 ml of benzene and inhibitor was added. This was thoroughly mixed, forming a slurry, and then refrozen. At the time of analysis the frozen mixture was allowed to warm up until the part of it in contact with the tube had thawed. The entire mixture was transferred to a centrifuge tube containing inhibitor. The original reaction tube was rinsed once more with 0.5 ml of benzene and the washing was added to the centrifuging tube. The tube was centrifuged and the solvent decanted. The residue was swollen with benzene and washed with methanol three times and finally vacuum dried. The radioactivity assay technique was used as previously described [5, 6]. Data are given in Tables 1-4 and Figs. 1-4.

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