Copolymerization Parameters of Itaconic Anhydride in Free-Radical Polymerization

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ABSTRACT

The copolymerization of itaconic anhydride (M_1) with four different monomers (M_2), namely: vinyl acetate, 2-chloroethyl acrylate, acrylonitrile, and styrene, was studied. Values of r_1 and r_2 were determined for copolymerizations in benzene and for two of these systems, namely those with vinyl acetate and 2-chloroethyl acrylate. Values of r_1 and r_2 were also determined for copolymerizations in tetrahydrofuran. The value of r_1 ranged from 0.53 to 4.8, but it was always very much greater than r_2. The Q-e values for itaconic anhydride in all the systems studied were also calculated and the average values for $Q_1 = 8.2$, $e_1 = 1.45$ were determined.

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*Taken in part from the dissertation submitted by Moustafa Sharabash in partial fulfillment of the degree of Doctor of Philosophy.

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INTRODUCTION

The first publication on itaconic anhydride as a monomer was by Drougas and Guile in 1961 [1]. They demonstrated that itaconic anhydride is an active monomer both in homopolymerization and copolymerization with styrene. Nagai et al. [2] reported on the co-polymerization of itaconic anhydride with several monomers but gave no definite values for the reactivity ratios of the anhydride in the systems studied. A cation exchange resin has been prepared from the poly(itaconic anhydride) by using diallyl itaconate as crosslinking agent [3].

The purpose of this investigation was to study, in greater detail, the free-radical copolymerization of itaconic anhydride with various vinyl and acrylic monomers, and to determine the reactivity ratios for further copolymerizations involving the anhydride. Comonomers of different polarities were chosen, namely; vinyl acetate, 2-chloro-ethyl acrylate, acrylonitrile, and styrene, in order to get reactivity ratios values that can be used in calculating and determining a Q-e value for the itaconic anhydride.

EXPERIMENTAL

The copolymerizations were carried out in benzene in which the polymer precipitates as it forms, or in tetrahydrofuran, in which the polymer remained in solution and was precipitated by a nonsolvent. All-glass equipment was used, and an improved polymerization technique [4] involving a sweeping process to free the reaction mixture from any traces of molecular oxygen was employed. Copolymerizations were carried out under nitrogen atmosphere, and the reaction was allowed to continue until the desired amount of polymer (about 5%) was obtained. The copolymer was quantitatively isolated and dried under vacuum (0.2 Torr at 56°C). The copolymer was analyzed for composition by either elemental analysis or by infrared analysis [5] or both.

Copolymerization in Benzene

Weighed amounts of monomers were dissolved in a quantity of an-hydrous, thiophene-free benzene sufficient to make the total molarity equal to 0.8 M. The calculated amount of initiator concentration was 0.2% (w/v). The reaction mixture was stirred until all components were dissolved. It was then subjected to the sweeping process mentioned above. The temperature was kept at 70 ± 2°C.

After the desired amount of polymer was formed, the reaction mixture was quickly cooled in Dry Ice-acetone bath. The polymer was isolated by centrifugation and washed several times with hot benzene. It was then dried and analyzed.

Copolymerization in Tetrahydrofuran

The copolymerization was carried out in anhydrous tetrahydrofuran at $64 \pm 2°C$. The experimental procedure was the same as that already described, with the following exceptions.

After quenching the reaction in the Dry Ice-acetone bath, the reaction mixture was concentrated by distilling off the tetrahydrofuran under vacuum at room temperature ($25°C$). The concentrated reaction mixture was stored in a refrigerator for 24 hr where the unreacted itaconic anhydride crystallized out. This treatment was used to remove excess itaconic anhydride that would be precipitated together with the polymer. The polymer was precipitated by using anhydrous diethyl ether and separated by centrifugation. It was washed several times with diethyl ether and then with hot benzene, dried, and analyzed.

Calculation of the Reactivity Ratios

The r_1 and r_2 values were calculated by using the copolymerization equation [6]:

$$r_2 = \frac{M_1}{M_2} \left[\frac{m_2}{m_1} \left(1 + \frac{M_1}{M_2} r_1 \right) - 1 \right] \tag{1}$$

This gave a series of the usual straight-line plots of r_1 vs. r_2. The graphical solution of the copolymerization equation gave the values of the reactivity ratios for each system.

Calculation of the Q-e Values

Q and e values were calculated by Eqs. (2) and (3).

$$e_1 = e_2 \pm (- \ln r_1 r_2)^{1/2} \tag{2}$$

$$Q_1 = (Q_2/r_2) \exp\{- e_2 (e_2 - e_1)\} \tag{3}$$

TABLE 1. Reactivity Ratio Data for Itaconic Anhydride–Vinyl Acetate Copolymerization

Expt. No.	Mole fraction M_1	In benzene		In tetrahydrofuran	
		Conversion (%)	Mole fraction m_1	Conversion (%)	Mole fraction m_1
1	0.1	3.57	0.535	5.40	0.395
2	0.2	3.91	0.652	4.59	0.535
3	0.3	5.59	0.720	5.88	0.640
4	0.4	4.44	0.775	5.89	0.705
5	0.5	2.32	0.807	5.33	0.775
6	0.6	3.51	0.863	4.41	0.800
7	0.7	3.52	0.882	3.91	0.824
8	0.8	3.32	0.923	5.01	0.873
9	0.9	5.22	0.960	6.00	0.923

RESULTS

In this paper, M_1 refers to itaconic anhydride in the reaction mixture, m_1 refers to itaconic anhydride moiety in copolymer, and r_1 refers to the reactivity ratio for itaconic anhydride.

Copolymerization of Itaconic Anhydride and Vinyl Acetate

The itaconic anhydride–vinyl acetate (IA-VA) system was studied in benzene as well as in tetrahydrofuran. The copolymer compositions were determined by using infrared analysis. The reactivity ratio data are found in Table 1. The copolymer composition curves are shown in Fig. 1, and the graphical solutions of the copolymerization equation are shown in Figs. 2 and 3.

Copolymerization of Itaconic Anhydride and 2-Chloroethyl Acrylate

The itaconic anhydride–2-chloroethyl acrylate (IA-2ClEA) system was also studied in benzene and in tetrahydrofuran. The copolymer
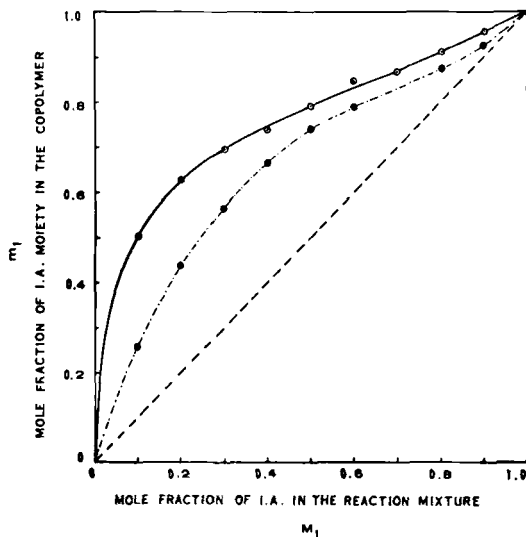
FIG. 1. Composition curve of IA-VA copolymerization: (o—) in benzene; (●•—•) in THF.
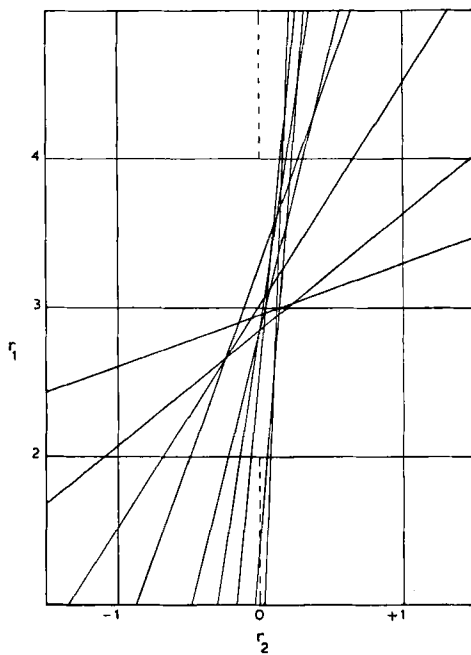
FIG. 2. Graphical solution of copolymerization equation for IA-VA copolymerization in benzene.
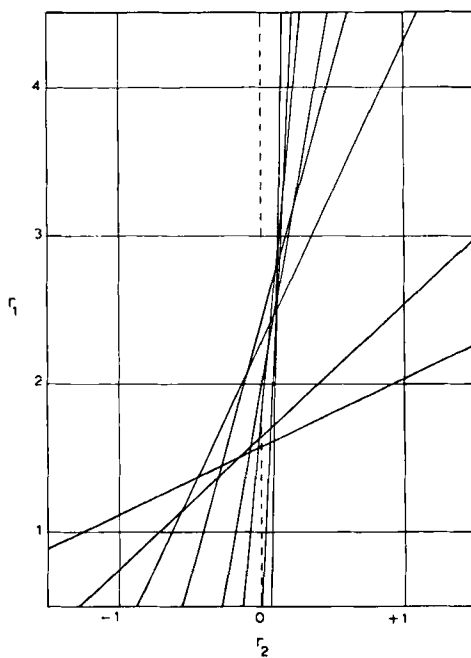

FIG. 3. Graphical solution of copolymerization equation for IA-VA copolymerization in THF.

composition for those copolymers obtained in benzene was determined by both elemental analysis for chlorine content and by quantitative infrared analysis. The copolymers obtained in tetrahydrofuran were analyzed by using infrared analysis only. The reactivity ratio data are found in Table 2. The copolymer composition curves are shown in Fig. 4, and the graphical solutions of the copolymerization equation for this system are shown in Figs. 5 and 6.

Copolymerization of Itaconic Anhydride and Acrylonitrile

The itaconic anhydride–acrylonitrile (IA-AN) system was studied in benzene. The copolymer compositions were determined by elemental analysis for nitrogen. The reactivity ratio data are found in Table 3. The copolymer composition curve is shown in Fig. 7, and the graphical solution of the copolymerization equation is shown in Fig. 8.

Copolymerization of Itaconic Anhydride and Styrene

The itaconic anhydride–styrene (IA-S) system was studied in benzene. The copolymer compositions were determined by elemental
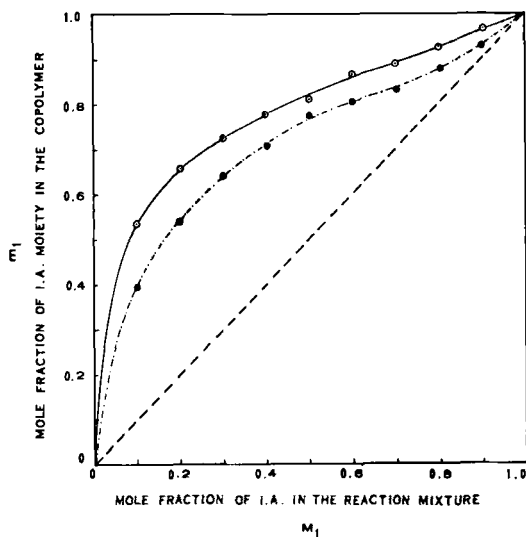

FIG. 4. Composition curve of IA-2ClEA copolymerization: ($\circ$—) in benzene; ($\bullet$·–·) in THF.

TABLE 2. Reactivity Ratio Data for Itaconic Anhydride–2–Chloroethyl Acrylate Copolymerization

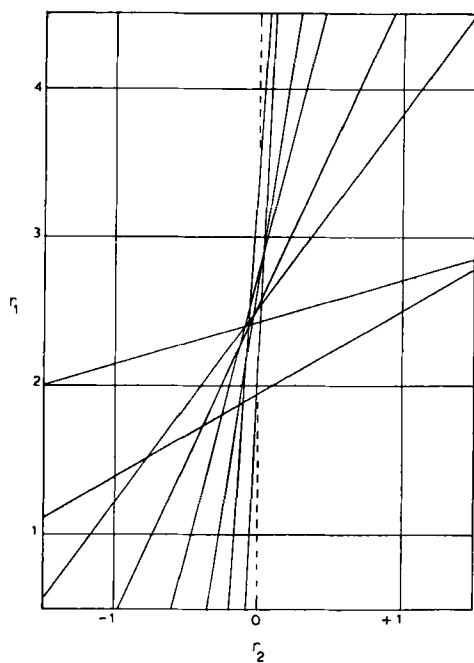| Expt. No.	Mole fraction M_1	In benzene		In tetrahydrofuran	
		Conversion (%)	Mole fraction m_1	Conversion (%)	Mole fraction m_1
1	0.1	3.50	0.506	6.00	0.262
2	0.2	2.70	0.633	7.28	0.444
3	0.3	2.70	0.700	5.80	0.565
4	0.4	6.50	0.737	5.42	0.671
5	0.5	4.83	0.792	6.04	0.745
6	0.6	5.09	0.847	4.76	0.792
7	0.7	4.70	0.863	–	–
8	0.8	4.50	0.908	4.05	0.872
9	0.9	5.90	0.945	2.59	0.924

FIG. 5. Graphical solution of copolymerization equation for IA-
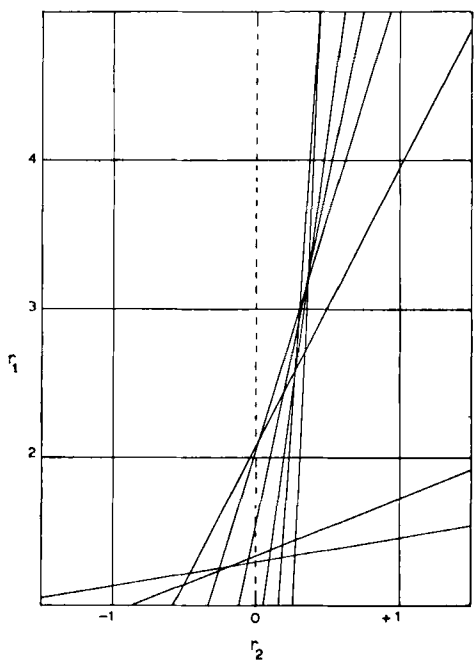2ClEA copolymerization in benzene.

FIG. 6. Graphical solution of copolymerization equation for IA-
2ClEA copolymerization in THF.

TABLE 3. Reactivity Ratio Data for Itaconic Anhydride–Acrylonitrile Copolymerization in Benzene

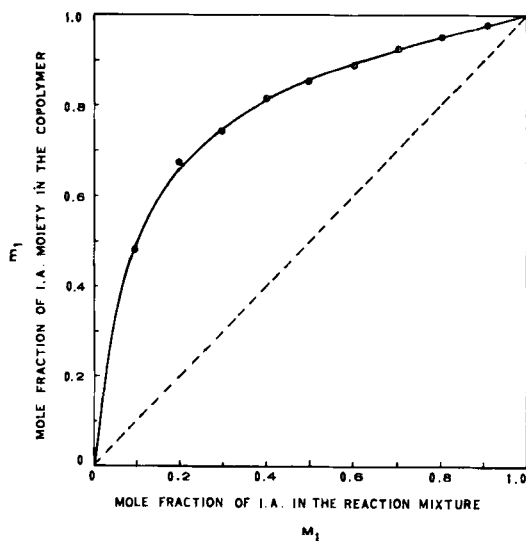| Expt. No.	Mole fraction M_1	Conversion (%)	Mole fraction m_1
1	0.1	3.88	0.48
2	0.2	4.54	0.67
3	0.3	4.78	0.74
4	0.4	3.56	0.81
5	0.5	4.50	0.85
6	0.6	5.57	0.88
7	0.7	5.25	0.92
8	0.8	5.75	0.95
9	0.9	6.00	0.97

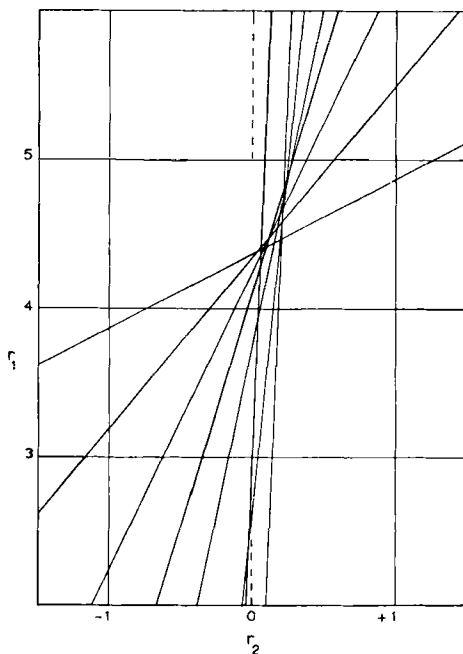FIG. 7. Composition curve of IA–AN copolymerization in benzene.

FIG. 8. Graphical solution of copolymerization equation for IA-AN copolymerization in benzene.

analysis for carbon. The reactivity ratio data are shown in Table 4. The copolymer composition curve is shown in Fig. 9, and the graphical solution of the copolymerization equation is shown in Fig. 10. The calculated reactivity ratios for these systems are shown in Table 5.

Q-e Scheme

The values for the Q-e scheme for itaconic anhydride were calculated according to Eqs. (2) and (3), and are shown in Table 6. The values for the comonomers (Q_2-e_2) were obtained from the literature [7]. The average Q-e values for itaconic anhydride were determined by plotting log Q_1 vs. e_1. The lines, except for the vinyl acetate system, intersected almost at one point, as shown in Fig. 11. The values for $Q_1 = 8.2$ and $e_1 = 1.45$ corresponding to the point of intersection, represent the average values for itaconic anhydride.

TABLE 4. Reactivity Ratio Data for Itaconic Anhydride–Styrene
Copolymerization in Benzene

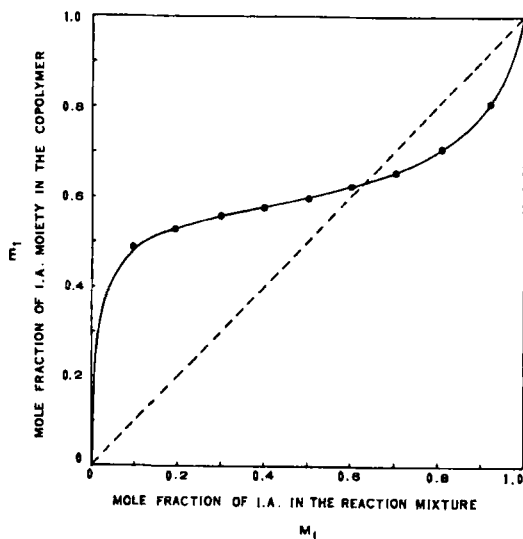| Expt. No.	Mole fraction M_1	Conversion (%)	Mole fraction m_1
1	0.1	2.40	0.48
2	0.2	4.29	0.52
3	0.3	6.70	0.55
4	0.4	5.22	0.56
5	0.5	5.83	0.59
6	0.6	5.60	0.61
7	0.7	4.88	0.65
8	0.8	6.80	0.70
9	0.9	5.00	0.78

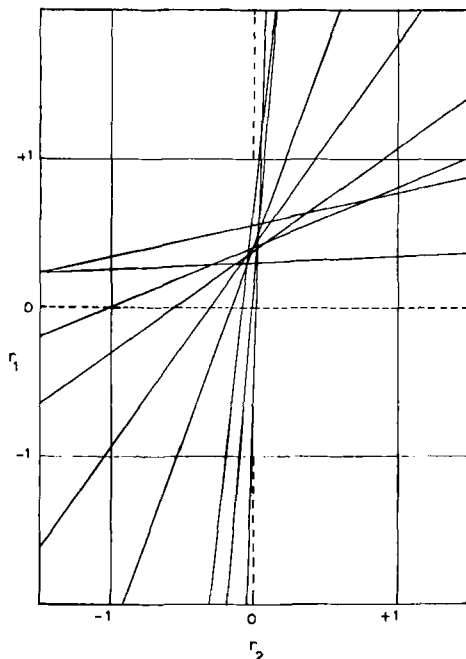FIG. 9. Composition curve of IA–S copolymerization in benzene.

FIG. 10. Graphical solution of copolymerization equation for IA-S copolymerization in benzene.

DISCUSSION

From the data shown in Table 5, it can be seen that itaconic anhydride is a very active monomer in free-radical polymerizations, in contrast to maleic anhydride [8], itaconic acid [9], and alkyl itaconates [10].

This confirms the findings of Drougas and Guile [1]. The high relative reactivity can be explained by the fact that the itaconic anhydride gives a tertiary radical which forms easily and is also a very reactive species. The $r_1 r_2$ products indicate that itaconic anhydride copolymers tend to alternate. Of the systems studied, itaconic anhydride–styrene copolymers are the most highly alternating. It is also the only system that forms an azeotrope.

A basic assumption in the derivation of the copolymerization equation was that the reactivity ratios are unaffected in most cases by the presence of inhibitors, chain transfer agents, or solvents [11-13].

TABLE 5. Reactivity Ratios of Itaconic Anhydride

Comonomer (M_2)	In benzene			In tetrahydrofuran		
	r_1	r_2	$r_1 r_2$	r_1	r_2	$r_1 r_2$
Vinyl acetate	3.08 ± 0.1	0.07 ± 0.02	0.2156	2.3 ± 0.2	0.1 ± 0.03	0.2300
2-Chloroethyl-acrylate	2.42 ± 0.1	0.08 ± 0.02	0.1936	3.1 ± 0.1	0.32 ± 0.04	0.992
Acrylonitrile	4.8 ± 0.2	0.13 ± 0.02	0.624			
Styrene	0.53 ± 0.1	0.018 ± 0.003	0.0095			

TABLE 6. Q-e Values for Itaconic Anhydride

Comonomer	Q	e	Solvent
Vinyl acetate	00.283	1.017	Benzene
	00.200	0.992	THF
2-Chloroethyl-acrylate	10.159	1.824	Benzene
	01.344	0.629	THF
Acrylonitrile	10.460	1.880	Benzene
Styrene	09.680	1.370	Benzene
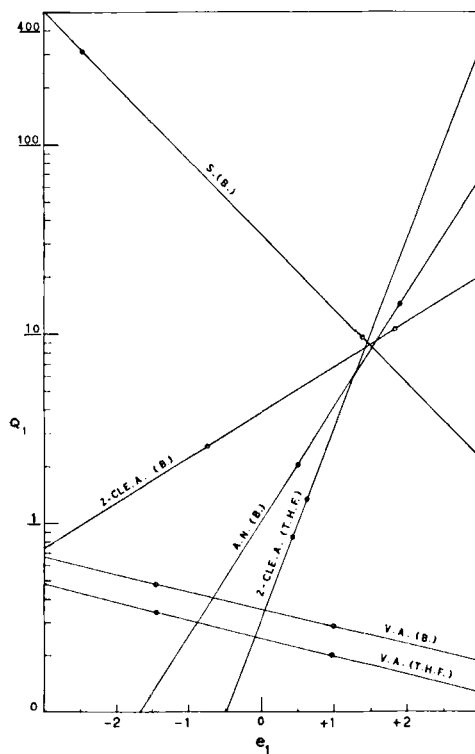
FIG. 11. Semilogarithmic plot of Q_1 vs. e_1.

However, there is a noticeable difference between the values obtained with tetrahydrofuran and those obtained when benzene was used as a solvent. This can be attributed to the insolubility of these copolymers in benzene. The monomer concentration of the individual monomers in the vicinity of the radicals on the precipitated polymer particles will be altered due to the difference in the degree of adsorption of the monomers on the particle surface.

The Q values calculated reflect the high activity of this monomer, and the positive e value is in agreement with fact that itaconic anhydride has an electron-poor double bond due to the neighboring carbonyl group.

ACKNOWLEDGMENTS

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