Relative Reactivity Ratios for Two New 2-Chloro-1,3-Butadiene Systems

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Synopsis

The relative reactivity ratios in free-radical, emulsion copolymerizations for the systems 2-chloro-1,3-butadiene/methyl isopropenyl ketone and 2-chloro-1,3-butadiene/methacrylic acid were found to be 3.6 and 0.1 and 2.68 and 0.15, respectively. Consequently, copolymers are formed substantially richer in 2-chloro-1,3-butadiene units than the comonomer feed, have little alternation tendency, and do not form azeotropes. Distributions of monomer units in the copolymers are described.

INTRODUCTION

The high relative reactivity of 2-chloro-1,3-butadiene in free-radical copolymerization with other dienes or activated olefins has been reported in both oil phase and emulsion systems.[1,2] This paper describes the measurement of the relative reactivity ratios of 2-chloro-1,3-butadiene/methyl isopropenyl ketone and 2-chloro-1,3-butadiene/methacrylic acid monomer mixtures.

EXPERIMENTAL MATERIALS AND METHODS

Monomers

The 2-chloro-1,3-butadiene (chloroprene) was distilled from a 50% mixture with xylene (b.p. 59°C., n_D^{20} 1.4578) and stored under nitrogen below $-20°C$. without stabilization. The active oxygen content at reaction time was 10–20 ppm. The methyl isopropenyl ketone (MIPK) was freed from stabilizer and dimer by distillation. The fraction boiling at 29°C. (50 mm. Hg) was collected and stored below $-20°C$. Glacial methacrylic acid stabilized with 0.025% of p-methoxyphenol was employed without distillation. Analyses for carboxyl groups and unsaturation were made by titrating with standard solutions of base and bromine.

Apparatus

Polymerizations were carried out in four-necked round-bottomed flasks fitted with agitators, thermometers, nitrogen inlets, burets, and hydrometer holders. The conversions were followed by measuring the changes in specific gravities with hydrometers calibrated in thousandths of a point.

Polymerizations

All operations were carried out under nitrogen and the distilled water was purged with nitrogen before emulsification. Emulsion recipes employed are given in Table I. Since the methacrylate anion has been shown to be much less reactive in polymerization than the undissociated methacrylic acid,[3] the emulsion system for copolymerization of methacrylic acid was maintained at a pH of 2.5 or lower to keep the acid undissociated.

TABLE I
Emulsion Recipes

Material	Parts per hundred of monomer	
	A	B
2-Chloro-1,3-butadiene	100 − x	100 − x
Methyl isopropenyl ketone	x	—
Methacrylic acid	—	x
tert-Dodecyl mercaptan	1.5	—
Oleic acid	4.0	—
Distilled water	150	150
Lomar PW[a]	4.0	—
Sodium hydroxide	1.076	—
Ultrawet K[b]	—	2.0

[a] Sodium sulfonate of a naphthalene–formaldehyde condensation product supplied by Jacques Wolf.

[b] An alkylbenzene sodium sulfonate supplied by the Atlantic Refining Company.

Polymerizations were initiated at 40°C. by careful addition of a 5% solution of potassium persulfate. The internal temperature was maintained at $40 \pm 0.5°$C. by external cooling. As soon as the specific gravity rose at least 0.003 point, the copolymerizations were arrested by pouring the entire emulsion into methanol containing a trace of a polymerization inhibitor such as phenothiazine.

Purification of Analytical Samples

Copolymers of 2-chloro-1,3-butadiene and methyl isopropenyl ketone were purified by repeated extractions with acetone. Similar treatment of a polychloroprene control yielded a reference value of 39.4% chlorine. Copolymers of 2-chloro-1,3-butadiene and methacrylic acid were purified by double precipitation from tetrahydrofuran solutions, water being used as the nonsolvent. The copolymers were dried at room temperature *in vacuo*.

DISCUSSION OF RESULTS

Determination of Relative Reactivity Ratios

The usual assumptions have been employed concerning the kinetic chain length, the existence of a steady state, and the constancy of monomer feed

composition at low conversion.[4]   Furthermore, the presence of mercaptan modifier was assumed not to affect the relative reactivities.

Fineman and Ross[5] have derived the following expression which permits straightforward calculation of relative reactivity ratios r_1 and r_2 from copolymerization data:

$$\frac{f_1(1 - 2F_1)}{(1 - f_1)F_1} = r_2 + \left[\frac{f_1{}^2(F_1 - 1)}{(1 - f_1)^2F_1}\right]r_1 \tag{1}$$

where f_1 denotes the mole fraction of unreacted monomer M_1 in the feed and F_1 denotes the mole fraction of M_1 monomer units in the increment of copolymer formed at the initial stage of copolymerization.

Each value of f_1 was taken to be the mole fraction of 2-chloro-1,3-butadiene in the initial monomer feed mixture.   Each value of F_1 was obtained by analysis of the copolymer for chlorine.   The copolymer composition data for emulsion-copolymerized 2-chloro-1,3-butadiene and methyl isopropenyl ketone are given in Table II.   These data employed in eq. (1) yielded the straight line plot in Figure 1.   The slope of the line is 3.6 and represents r_1 (M_1 = 2-chloro-1,3-butadiene).   The intercept at the y axis gives r_2 (M_2 = methyl isopropenyl ketone) = 0.1.

The corresponding copolymer composition data for the emulsion copolymerization of 2-chloro-1,3-butadiene and methacrylic acid are contained in

TABLE II
Dependence of Copolymer Composition on Monomer Feed for the 2-Chloro-1,3-Butadiene/Methyl Isopropenyl Ketone System

Conversion, %	Chlorine in copolymer, %	Mole fraction of 2-chloro-1,3-butadiene	
		Feed (f_1)	Copolymer (F_1)
—	39.4	1.00	1.00
5.3	36.2	0.74	0.92
7.9	35.7	0.69	0.90
4.7	34.3	0.59	0.86
9.2	31.9	0.49	0.80
8.5	29.9	0.39	0.75
13.3	20.5	0.19	0.51

TABLE III
Dependence of Copolymer Composition on Monomer Feed for the 2-Chloro-1,3-Butadiene Methacrylic Acid System

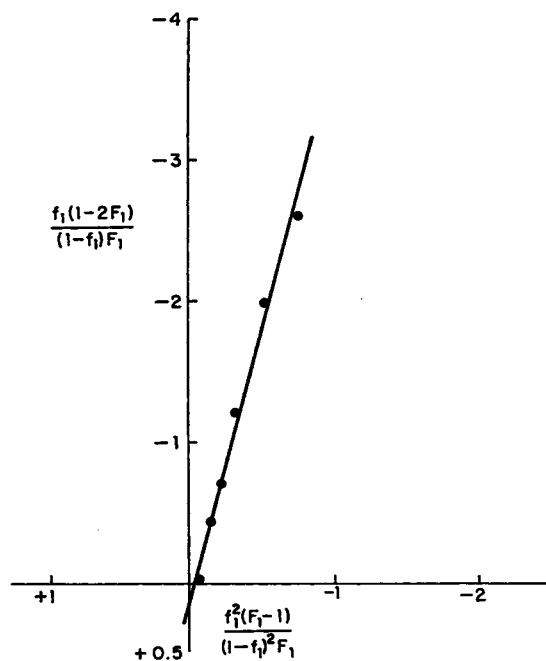| Conversion, %	Chlorine in copolymer, %	Mole fraction of 2-chloro-1,3-butadiene	
		Feed (f_1)	Copolymer (F_1)
5.07	38.4	0.898	0.958
3.48	36.8	0.795	0.918
1.21	34.7	0.694	0.865
3.25	33.2	0.587	0.826
3.72	27.4	0.393	0.681

Fig. 1. Relative reactivity plot for 2-chloro-1,3-butadiene/methyl isopropeny. ketone copolymerization. Slope = r_1 = 3.6 ± 0.2, y axis intercept = r_2 = 0.1 ± 0.05
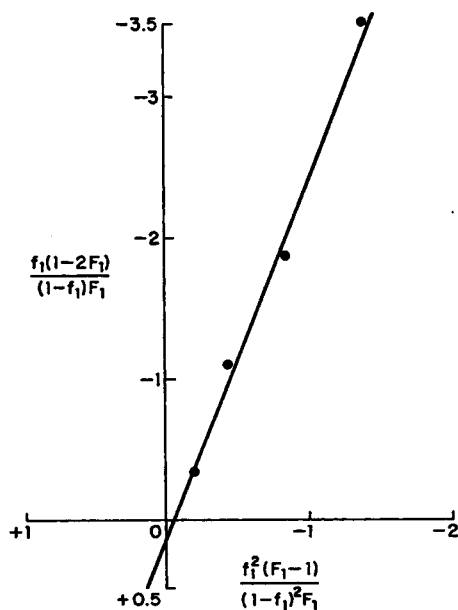

Fig. 2. Relative reactivity plot for 2-chloro-1,3-butadiene/methacrylic acid copolymerization. Slope = r_1 = 2.7 ± 0.2, y axis intercept = r_2 = 0.15 ± 0.05.

Table III. When employed in eq. 1, the above data yielded the straight line plot shown in Figure 2. From the slope r_1 is 2.7 (2-chloro-1,3-butadiene) and from the intercept at the y axis r_2 is 0.15 (methacrylic acid).

Detailed Structure of Copolymer Chains

In both cases the copolymers were formed relatively richer in 2-chloro-1,3-butadiene than the comonomer feed. This is a consequence of the preference of both 2-chloro-1,3-butadiene radical $(m_1\cdot)$ and methyl isopropenyl ketone or methacrylic acid radical $(m_2\cdot)$ for 2-chloro-1,3-butadiene (M_1) monomer. The arrangements of the monomer units in the copolymers are also similar. Copolymerization azeotropes are unlikely since both r_1 and r_2 are not greater than unity or less than unity. The alternation tendency is small since r_1 and r_2 are not simultaneously close to zero.

The distributions of the sequence lengths of 2-chloro-1,3-butadiene and methyl isopropenyl ketone or methacrylic acid units were calculated by known methods[6] for copolymers prepared from equimolar monomer mixtures. These are shown in Tables IV and V.

TABLE IV
Distribution of Sequence Lengths in Copolymer From Equimolar Monomer Mixture
(2-Chloro-1,3-Butadiene/Methyl Isopropenyl Ketone)

Units per sequence	% of 2-Chloro-1,3-butadiene sequences	% of MIPK sequences
1	21.8	90.9
2	17.1	8.26
3	13.3	0.75
4	10.4	0.068
5	8.2	0.0962
>5	29.2	0.0158

TABLE V
Distribution of Sequence Lengths in Copolymer From Equimolar Monomer Mixture
(2-Chloro-1,3-Butadiene/Methacrylic Acid)

Units per sequence	% of 2-chloro-1,3-butadiene sequences	% of methacrylic acid sequences
1	27.2	87.0
2	19.8	11.3
3	14.4	1.48
4	10.5	0.19
5	7.6	0.025
>5	20.5	0.005

Less than 1% of the methyl isopropenyl ketone sequences contain more than two monomer units, whereas over 60% of the 2-chloro-1,3-butadiene sequences contain more than two monomer units. Similarly, only 1.7% of the methacrylic acid sequences contain more than two monomer units,

whereas 53% of the 2-chloro-1,3-butadiene sequences contain more than two monomer units. Thus both copolymers are elastomers resembling in properties the homopolymer of 2-chloro-1,3-butadiene.

Infrared spectra confirm that 2-chloro-1,3-butadiene units in the copolymers are present in all possible modes of addition, and that these structures are present in the same ratio as in the homopolymer prepared at the same temperature.

Comparison with Other 2-Chloro-1,3-butadiene Copolymerizations

The relative reactivities obtained show the same high reactivity for 2-chloro-1,3-butadiene as do previously reported copolymerizations shown in Table VI. Alternation is reported only with the highly polar vinylidene cyanide.[11]

TABLE VI
Relative Reactivity Ratios with 2-Chloro-1,3-butadiene (M_1)

Comonomer (M_2)	r_1	r_2	Reference
Styrene	6.3 ± 0.1	0.00	1
Styrene	7 ± 2	0.05 ± 0.02	7
Styrene	8.11 ± 0.34	0.053 ± 0.005	8
Butadiene	3.41 ± 0.07	0.059 ± 0.015	1
Isoprene	3.65 ± 0.11	0.133 ± 0.025	1
Acrylonitrile	6.07 ± 0.53	0.01 ± 0.1	1
Acrylonitrile	5.35 ± 0.2	0.045 ± 0.004	8
Methyl methacrylate	6.12 ± 0.2	0.08 ± 0.007	8
Methyl acrylate	11.1 ± 1.5	0.078 ± 0.01	8
1,1-Diphenylethylene	3.2 ± 0.2	0.0 ± 0.05	8
Isopropyl vinyl ether	11.45	0.164	9
Vinylpyridine	5.195	0.064	10
Vinylquinoline	2.1	0.38	10
Diethyl fumarate	6.65 ± 0.37	0.027 ± 0.009	8
Vinylidene cyanide	0.016	0.0048	11
Vinyl formate	30	0.01	13

The Q and e values for 2-chloro-1,3-butadiene, based on its copolymerization with butadiene,[1] are calculated to be 8.07 and 0.46, respectively. The reported Q and e values for methacrylic acid[12] are 2.0 and 0.7, respectively. Based on the copolymerization of vinylidene chloride and methyl isopropenyl ketone,[12] the Q and e values for methyl isopropenyl ketone are 1.95 and 1.23, respectively. Thus, the calculated relative reactivities for 2-chloro-1,3-butadiene/methacrylic acid are 4.5 and 0.21, and for 2-chloro-1,3-butadiene/methyl isopropenyl ketone are 5.9 and 0.094, in fair agreement with the experimental values.

The high Q value of 2-chloro-1,3-butadiene indicates the strong tendency of the monomer to add to radicals. The relatively neutral e value permits the radical to react with only small alternating tendencies with both electron-releasing and electron-attracting substituents in the comonomer.

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Résumé

On a étudié les rapports de réactivité relative des systèmes 2-chloro-1,3-butadiène-méthylisopropénylcétone et 2-chloro-1,3-butadiène acide méthacrylique au cours de leur copolymérisation en émulsion en présence de radicaux libres. Ces valeurs s'élèvent respectivement á 3.6 et 0.1, et 2.7 et 0.15. Par conséquent, les copolymères formés sont considérablement enrichis en unités de 2-chloro-1,3-butadiène comparés au mélange des comonomères de départ. Il y a peu de tendance á l'alternance et aucun azéotrope n'est formé. On a donné des détails sur la distribution des unités de monomères au sein des copolymères.

Zusammenfassung

Die relativen Reaktivitätsverhältnisse für die radikalische Emulsionscopolymerisation der Paare 2-Chlor-1,3-butadiene-Methylisopropenylketon und 2-Chlor-1,3-butadien-Methacrylsäure wurden zu 3,6 und 0,1 bzw. 2,7 und 0,15 bestimmt. Demzufolge enthalten die Copolymeren wesentlich mehr 2-Chlor-1,3-butadien-Einheiten als die vorgegebene Monomermischung, zeigen geringe Alternationstendenz und bilden kein Azeotrop. Die Verteilung der Monomereinheiten in den Copolymeren wird beschrieben.