[Contribution from the Noyes Chemical Laboratory, University of Illinois]

REACTIVITY RATIOS OF CHLORINATED STYRYL CARBONYL DERIVATIVES WITH 1,3-BUTADIENE

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Although chalcones and cinnamate esters are among the most familiar organic compounds, it is only very recently that their possible importance as monomers or comonomers has received any detailed attention. Reports published within the past few years have shown that the ability of both classes of compounds to copolymerize with various monomers is rather general (1–3) and that some cinnamate esters can also homopolymerize (4). Copolymers of these compounds with butadiene are of special interest since butadiene-chalcone copolymers have shown promise as elastomers for useful synthetic rubbers (1). Thus far, however, no quantitative measures of reactivity have been reported for any of these monomers. It was therefore considered of interest to determine some reactivity ratios for representatives of these types with butadiene.

The determination of reactivity ratios requires a reasonably precise and reliable method for the determination of monomer incorporation. In the case of butadiene copolymers calculation of incorporation from oxygen percentage has often been found unsatisfactory presumably because of a small oxygen uptake from the air during manipulation. However, the effect of this uptake on analysis for other elements such as chlorine is considerably less. Three "chlorine labeled" compounds were therefore chosen as representatives of the styryl carbonyl derivatives, namely: 2-chlorobenzalacetophenone, methyl 2-chlorocinnamate, and methyl 4-chlorocinnamate.

Reactivity ratios are supposedly unaffected by the presence of a solvent or by the nature of the initiator (5); however, bulk reactions initiated by benzoyl peroxide were preferred in this study because of their simplicity and convenience. In the case of 2-chlorobenzalacetophenone, a series of polymers was also prepared in emulsion for comparison. Both bulk and emulsion runs involving 2-chlorobenzalacetophenone were made near 60° since this monomer does not form homogeneous systems with butadiene over the desired concentration range if the temperature is much lower than this; whereas the emulsion polymerization would be too rapid if the temperature were much higher. Polymerizations involving methyl 4-chlorocinnamate (m.p. 76°) had to be run at 80° to obtain homogeneous systems. Methyl 2-chlorocinnamate polymerizations were run at both 60° and 80° so that they could be better compared with each of the other two.

Significant data for each series of polymers prepared are listed in Tables I and II. When product mole ratios (m_2/m_1)[1] and charge mole ratios (M_1/M_2)

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[1] m_2/m_1 is the approximation of the differential ratio $\frac{dm_2}{dm_1}$ obtained by determining the product mole ratio at low conversion. In this paper subscript 1 will always refer to butadiene.

TABLE I

REACTIVITY RATIO DATA OBTAINED FROM BULK COPOLYMERIZATIONS OF BUTADIENE WITH STYRYL CARBONYL MONOMERS

Charge Mixture					Time, Hrs.	Product				Mole Ratio corrected[h]
Sample No.	Wt. of Diene, g.	Wt. of Styryl Cpd. g.	Mole Ratio (M_1/M_2)[a]	Benzoyl Peroxide, g.		Yield, g.	Conversion, %[b]	% Cl in Product	Mole Ratio (m_2/m_1)[c]	
Bulk Copolymerizations of 2-Chlorobenzalacetophenone and Butadiene 59.0°										
P-14-1	1.416	18.89	0.037	0.020	2.9	0.57	9	11.19 11.28[d]	0.738[e]	
P-14-2	1.805	15.19	.535	.015	2.9	.37	5	10.96	.667	
P-14-3	2.82	11.42	1.108	.009	2.9	.26	3	10.20	.513	
P-14-4	3.73	7.75	2.16	.007	2.9	.15	1.5	9.28	.386	
Bulk Copolymerizations of Methyl 2-Chlorocinnamate and Butadiene (Polymerizations Run at 60°)										
P-50b	2.48	11.12	.811	.020	4.7	.31	4	11.72	.511	
P-56-1	4.53	3.46	4.76	.023	6.1	.14	2	6.87	.145	
P-56-2	0.696	7.81	.325	.022	6.1	.34	13	31.18	.747	
P-56-5	4.56	8.41	1.972	.028	6.1	.32	3	9.69	.318	
(Polymerizations Run at 80°)										
P-81-1	5.83	6.62	3.21	.021	2.0	.6	6	7.54	.197	
P-81-2	4.08	11.15	1.332	.020	2.0	.75	8	10.20 9.94[d]	.346[e]	
P-81-5	2.53	14.12	.652	.025	1.2	.95	13	11.72	.510	
P-81-6	6.48	6.14	3.83	.027	2.0	.35	3	7.14	.180	
Bulk Copolymerizations of Methyl 4-Chlorocinnamate and Butadiene at 80° (Series A)[f]										
P-77-1	3.22	14.62	.802	.026	2.0	.45	6	10.26	.361	0.268[h]
P-77-4	4.27	10.37	1.497	.026	2.0	.53	6	8.86	.264	0.1848[h]
P-77-7	1.742	11.42	.554	.026	2.0	.52	11	11.56	.488	0.375[h]
P-77-8	8.98	4.28	7.65	.026	2.0	.12	1	5.04	.106	0.0502[h]
P-77-9	4.24	7.25	2.13	.026	1.5	.36	5	8.40 7.97[d]	.234[e]	0.1550[h]
(Series B)[g]										
P-97-1	6.73	3.79	6.47	.025	2.0	.32	4	5.14	.1095	0.0527[h]
P-97-2	4.55	6.03	2.75	.016	2.0	.40	5	7.29	.1858	0.1182[h]
P-97-3	5.04	10.45	1.750	.017	3.2	.50	5	8.48	.244	0.1672[h]
P-97-4	4.28	13.76	1.130	.019	3.2	.50	5	9.75 9.93[d]	.343[e]	0.246[h]

[a] Mole ratio of diene/ketone or diene/ester in the charge mixture (M_1/M_2).

[b] Per cent conversion based on the weight of the most depleted monomer incorporated in the product.

[c] Mole ratio of ketone/diene or ester/diene incorporated in the product polymer, (m_2/m_1).

[d] Second analysis carried out on the same sample after precipitating it one or two extra times to check the effectiveness of purification.

[e] Mole ratio based upon the arithmetic mean of the two chlorine analyses.

[f] Samples for Series A were precipitated a total of four times in methanol at room temperature.

[g] Samples of Series B were precipitated once in methanol at room temperature and five times in boiling methanol.

[h] Values of m_2/m_1 corrected for the presence of impurity.

TABLE II

REACTIVITY RATIO DATA OBTAINED FROM EMULSION COPOLYMERIZATIONS OF BUTADIENE AND 2-CHLOROBENZALACETOPHENONE AT 60°

Sample No.	Recipe						Time of Reaction, hrs.	Conversion,[d] %	% Cl in Copolymer	Mole Ratio m_2/m_1[e]
	Wt. of Diene, g.	Wt. of Ketone, g.	Mole Ratio M_1/M_2[a]	$K_2S_2O_8$, g.	Soap Solution, ml.[b]	Modifier, g.[c]				
P-68-3	7.25	4.79	6.76	0.020	15	0.026	0.7	2.5	7.45	0.232
P-68-4	5.16	8.50	2.72	.030	20	.039	.7	5.6	8.91	.348
P-68-6	3.92	13.88	1.27	.040	30	.039	1.2	8.3	9.86	.482
P-68-7	2.43	20.76	0.525	.041	40	.013	1.6	5.2	10.96	.671
P-68-12	3.66	16.90	0.671	.035	40	.013	1.7	8.7	10.32	.537

[a] Mole ratio of monomers in the reaction mixture (diene/ketone).

[b] OSR soap 5.0 g./170 ml. water.

[c] Dodecyl mercaptan.

[d] Per cent conversion is based upon the weight of the most depleted monomer incorporated in the copolymer.

[e] Mole ratio of monomers in the product (ketone/diene).

listed in the tables are substituted in the differential form of the copolymerization equation (5–6), $r_2 = \frac{M_1}{M_2}\left[\frac{m_2}{m_1}\left(1 + \frac{M_1}{M_2} r_1\right) - 1\right]$, linear equations containing the reactivity ratios, r_1 and r_2, are obtained.

These are solved graphically by the method of Lewis and Mayo (5). The values of r_1 and r_2 for 2-chlorobenzalacetophenone and methyl 2-chlorocinnamate as determined by the apparent common points of intersection in Figures 1 to 4 are listed in Table III.

The equations corresponding to the first series of copolymers (A) prepared from butadiene and methyl 4-chlorocinnamate are plotted in Figure 5. In this case nothing resembling a common point of intersection appears. Values of r_1 and r_2 at points of intersection tend to become lower as the ester incorporation decreases, the latter becoming more and more negative. This is the pattern to be expected in such a graph when one is dealing with a monomer pair having r_2

TABLE III

REACTIVITY RATIOS OF 1,3-BUTADIENE WITH STYRYL CARBONYL MONOMERS

Second Monomer	System	Temp., °C.	r_1	r_2
2-Chlorobenzalacetophenone	Bulk	59	0.78	−0.02
2-Chlorobenzalacetophenone	Emulsion	60	0.78	−0.04
Methyl 2-chlorocinnamate	Bulk	60	1.07	−0.02
Methyl 2-chlorocinnamate	Bulk	80	1.20	−0.03
Methyl 4-chlorocinnamate	Bulk	80	2.7[a]	0.0[a]

[a] As determined using the extrapolation procedure.

equal to zero if the analyses are made on products which all contain significant percentages of some impurity having a high chlorine content such as ester monomer or Diels-Alder adduct. The latter seems unlikely since no adduct could be isolated from a mixture of 5.65 g. of the ester and 7.47 g. of butadiene which

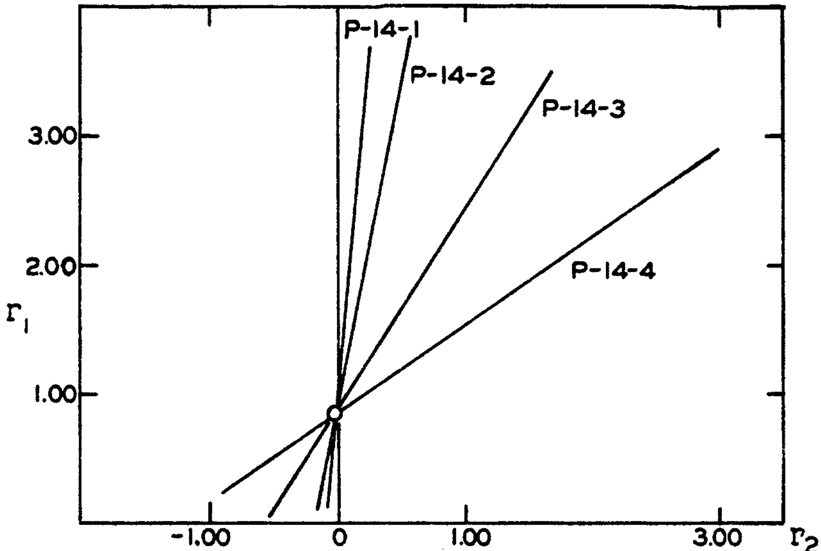


FIG. 1 REACTIVITY RATIO EQUATIONS FOR 2-CHLOROBENZALACETOPHENONE AND BUTADIENE AT 59°C (BULK)

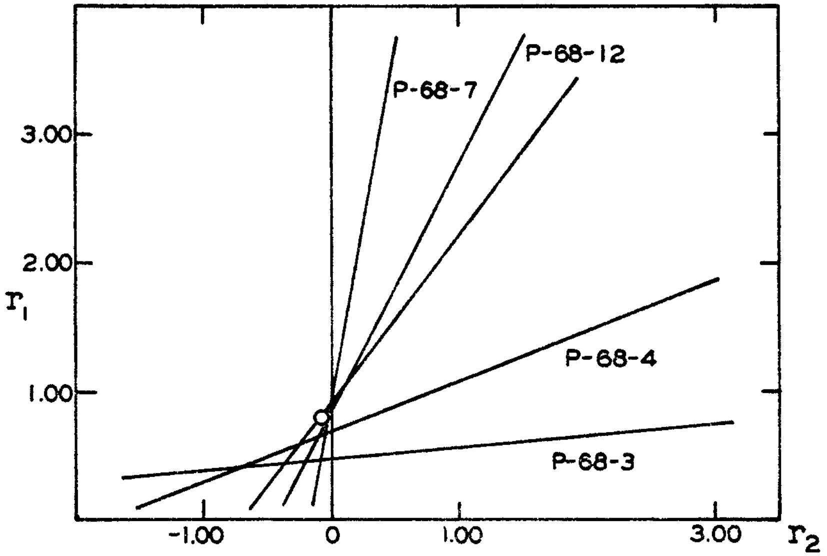


FIG. 2 REACTIVITY RATIO EQUATIONS FOR 2-CHLOROBENZALACETOPHENONE AND BUTADIENE AT 60°C. (EMULSION)

had been maintained at 80° for 14 hours (without initiator). On the other hand, it was considered not unlikely that some ester monomer might remain in the products even after four precipitations into methanol since its solubility is relatively less than the other two styryl derivatives. Comparison of the infrared spectra of ester and polymer was inconclusive; their carbonyl bands were too

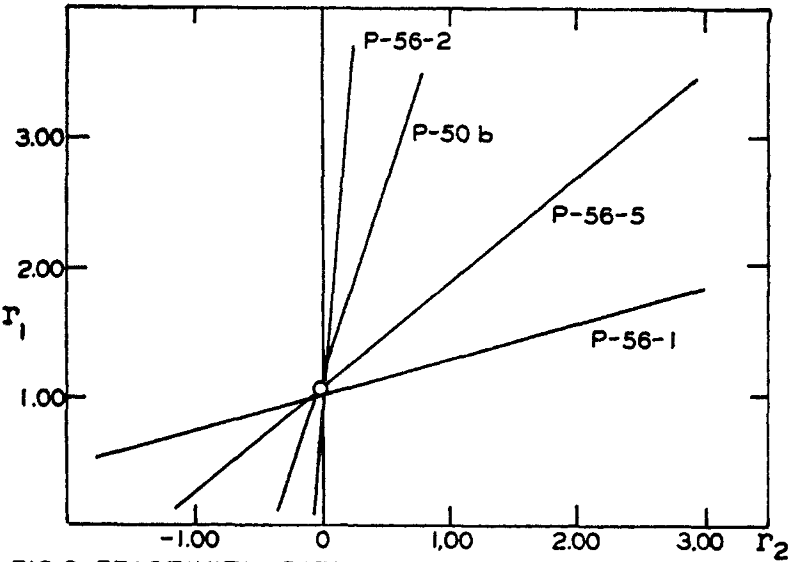


FIG. 3. REACTIVITY RATIO EQUATIONS FOR METHYL 2-CHLOROCINNAMATE AND BUTADIENE AT 60°C (BULK)

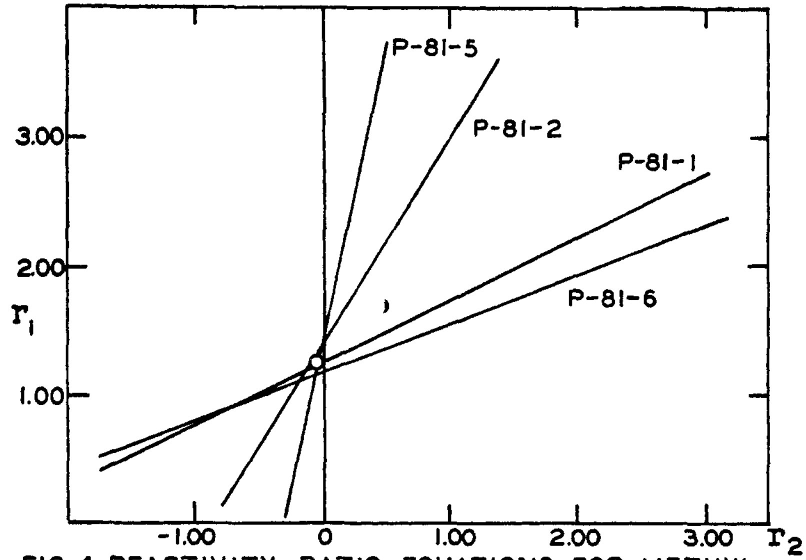


FIG. 4. REACTIVITY RATIO EQUATIONS FOR METHYL 5-CHLOROCINNAMATE AND BUTADIENE AT 80°C (BULK)

close together (1725 and 1736 cm.$^{-1}$ respectively). While the assumption that impurity is present is not absolutely certain, it should be pointed out that these deviations can not be accounted for on the basis of repulsion of penultimate, polar chain units for polar molecules as has been done in the case of styrene-fumaronitrile copolymers (7).

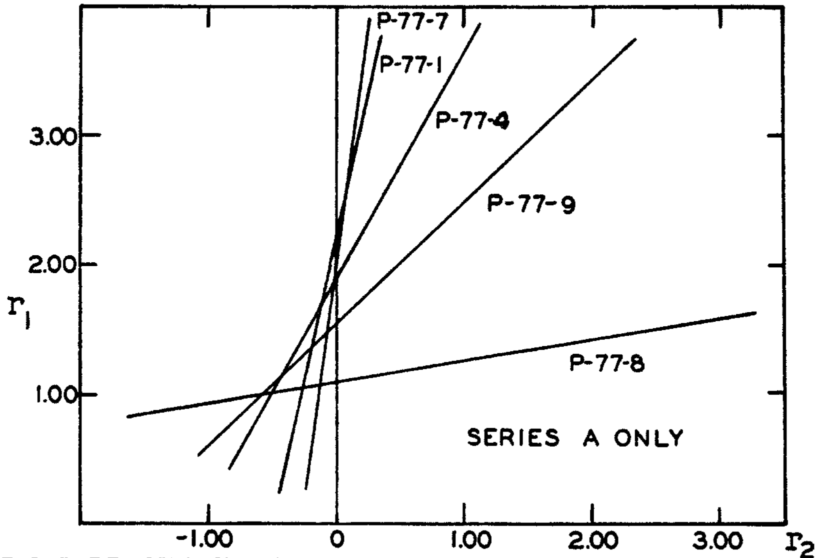


FIG. 5. REACTIVITY RATIO EQUATIONS FOR METHYL 4-CHLOROCINNAMATE AND BUTADIENE AT 80° C (BULK)

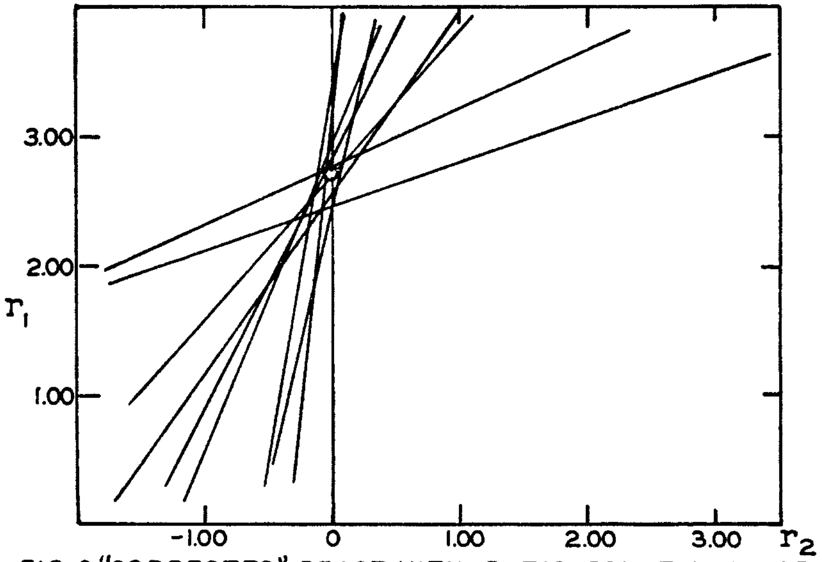
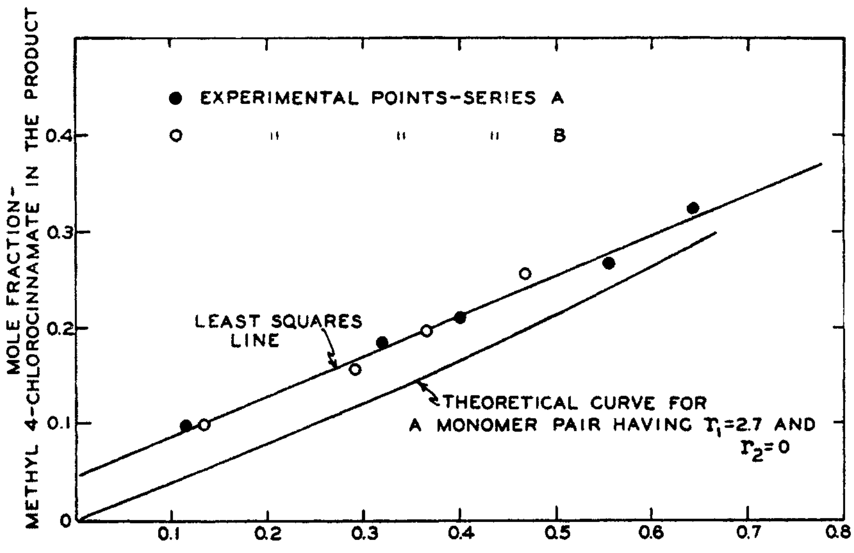


FIG. 6. "CORRECTED" REACTIVITY RATIO EQUATIONS FOR METHYL 4-CHLOROCINNAMATE AND BUTADIENE AT 80°C (BULK)



MOLE FRACTION OF METHYL 4-CHLOROCINNAMATE IN THE CHARGE
FIG. 7

In the hope of eliminating this difficulty, a second series (B) of four samples were run under the same conditions and purified by a total of six precipitations in methanol, the last five being precipitations in *boiling* methanol. Data on this series are also listed in Table I. However, it is found that when reactivity ratio equations are derived from this series and plotted, the results are approximately the same as in the previous series. Mole fractions of ester in the charge are plotted against mole fractions of ester in the products for both series in Figure 7. From this graph it is evident that no appreciable removal of impurity has been effected by the more drastic purification procedure used in series B; in fact a nearly linear relationship seems to hold for both series. It therefore seems reasonable to assume that a constant proportion of impurity, which cannot be removed by methanol precipitation, is probably present in all samples.[2] Attempts to find a satisfactory precipitant other than methanol were not successful. Linear extrapolation by the method of least squares leads to a value of 0.0454 for the mole fraction of ester presumably present in a polymer obtained from a charge containing no ester at all. This is equivalent to a chlorine percentage of 2.67.

On the basis that 2.67 per cent of the chlorine in each sample corresponds to impurity, a series of "corrected" values for m_2/m_1 are calculated and listed in Table I. Reactivity ratio equations calculated from the corrected values of m_2/m_1 are plotted in Figure 6. It is seen from this graph that the lines intersect approximately at a point corresponding to values of 2.7 for r_1 and 0.0 for r_2. It will be noted that the theoretical mole fraction curve for these "r" values, which is included in Figure 7, is nearly linear.

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[2] It is possible the impurity may consist of traces of ester homopolymer which formed after the butadiene had been removed in spite of precautions taken to prevent this. This homopolymer would be practically insoluble in methanol.

Estimates of the maximum errors involved in the "r" values listed in Table III can be made on the basis of the assumption that the maximum error in the chlorine analyses (about ±0.25%) is the primary limiting factor (*cf.* ref. 5, p. 22). In the cases of 2-chlorobenzalacetophenone and methyl 2-chlorocinnamate copolymers this leads to the conclusion that the maximum errors in r_1 and r_2 should not be greater than about ±0.12 and ±0.05 respectively. In the case of the methyl 4-chlorocinnamate copolymers the same assumption leads to estimated allowable errors of ±0.3 for r_1 and ±0.05 for r_2; however, in this latter case it is probable that some appreciable error also results from the extrapolation procedure; no estimate of this can be given.

It is of interest to note that the values of r_2 listed in Table III are essentially zero for all three systems. This means that the rate of reaction of growing chains ending in styryl carbonyl units with the styryl carbonyl molecules themselves is negligible compared with the rate of reaction of these chains with butadiene molecules. This is to be expected since these monomers may be regarded as 1,2-disubstituted ethylenes, which for steric reasons have little tendency to react with themselves. To be sure, it was found in the course of this work that methyl 4-chlorocinnamate like unsubstituted methyl cinnamate (4) can be made to homopolymerize (at 100–110°); however, it is not surprising that this reaction can not compete with the addition of these chains to the relatively unhindered butadiene molecules.

Methyl 2-chlorocinnamate failed to homopolymerize under conditions identical with those which succeeded with the 4-chloro and the unsubstituted esters. The difference probably results from the fact that the *ortho* chlorine atom tends to block the formation of the transition state for the chain growth reaction as can be demonstrated with Fischer-Taylor-Herschfelder models. In view of this, it is somewhat of a paradox to note that r_1 for the 2-chloro ester seems to be lower than for the 4-chloro ester (assuming r_1 for the 4-chloro ester is valid), indicating that the former is decidedly more active with respect to radicals ending in butadiene type units. This implies that steric factors do not play the predominant role in this step. The observed difference may be the result of the greater inductive effect or direct field effect of the relatively close *ortho* chlorine; this would tend to make the double bond more electron-poor, thereby enhancing its reactivity toward the electron-rich butadiene. A parallel effect has been noted in the copolymerization of *ortho* and *para* chlorostyrenes with styrene (8).

The increase of r_1 from 1.07 to 1.20 with a 20° rise in temperature is within the allowable experimental error and is probably not significant. The lower value of r_1 (and hence greater reactivity) of 2-chlorobenzalacetophenone is to be expected because the interaction of the carbonyl group with the double bond is not limited by cross-conjugation of a methoxyl group as in the esters. The same order of activity is noted on comparing the r_1 values for the methyl vinyl ketone-styrene system with the methyl acrylate-styrene system (5). The equality of the reactivity ratios of the 2-chlorobenzalacetophenone-butadiene system in bulk and emulsion is in accord with the findings of Smith and others (1) on systems in which neither monomer is particularly water-soluble.

In general the results of this study indicate that styryl carbonyl monomers have about the same order of activity as styrene ($r_1 \approx 1.4$) when copolymerizing with unhindered monomers.

EXPERIMENTAL[3]

Materials. Phillips Petroleum Company, "special purity grade" butadiene was used in all experiments. 2-Chlorobenzalacetophenone (m.p. 51.0–52.7°) was prepared as described by Bickel (9) and recrystallized twice from redistilled methanol. Methyl 2-chlorocinnamate ($n_D^{20.3}$ 1.5822) and methyl 4-chlorocinnamate (m.p. 75–76°) were prepared by refluxing dry methanol solutions of the corresponding acids while passing in hydrogen chloride for several hours. They were rendered analytically pure by repeated vacuum distillation. The emulsifier used in emulsion runs consisted of a 2.86 per cent solution of soap (Office of Synthetic Rubber specification L. M. 2.3.0.5.2). Other reagents were of pure commercial grades.

Procedure for bulk runs. Reactions were carried out in heavy-walled Pyrex tubes having 6–8 cm. constricted portions at the top (see ref. 5, p. 30). The tubes were of such size that relatively little free space existed above the charge. Styryl monomers were melted if necessary and poured in through special very narrow funnels. Benzoyl peroxide was added, the tubes were cooled in Dry Ice and the required amount of butadiene was admitted as a gas and condensed. Tubes were then allowed to warm until the butadiene began to boil, and again immersed in Dry Ice. The resulting slight vacuum within the tube allowed the narrow portion to be easily and effectively sealed with a hand torch. Tubes were carefully weighed before and after adding the styryl monomer and the initiator and again after the final sealing so that the weight of each component could be obtained by difference.

Tubes were then placed in a constant temperature bath maintained at the desired temperature ±0.8°. In the determinations using solid styryl monomers, it was necessary to shake each tube intermittently as it warmed until the mixture became homogeneous. This required from two to ten minutes. Each tube then was left in the bath as long as necessary to obtain, if possible, a two to ten per cent conversion. The time required for this had to be determined by preliminary trial runs.

At the end of each run tubes were cooled and opened. The contents of each was removed using as much benzene as necessary to dissolve any solid. The resulting solution was added dropwise to 100–200 ml. of stirred methanol containing about 0.1 g. of hydroquinone to inhibit any further polymerization and serve as a temporary antioxidant. The liquid was decanted,[4] and the product was dried in a vacuum one or two hours at 80° and weighed. The weight so obtained is referred to in the tables as the "yield".

Each sample then was purified further by dissolving it in the minimum convenient amount of benzene and adding it dropwise to about a ten-fold volume of stirred methanol. Two such additional precipitations were employed for each of the 2-chlorobenzalacetophenone and methyl 2-chlorocinnamate copolymers. Each of the set of samples of methyl 4-chlorocinnamate copolymer referred to as series "A" was precipitated three additional times, and each of the set of samples referred to as series "B" was precipitated five additional times using boiling methanol and decanting while hot. Each sample was prepared for analysis by dissolving in a few milliliters of benzene, filtering the solution and removing the benzene by vacuum sublimation at 0°. After allowing the samples to warm to room temperature and remain at a pressure of 1 mm. of Hg. for several hours, they were given a final drying under a vacuum at 80° for ten hours and then analyzed for chlorine. In certain cases, as noted in the tables, the same sample was analyzed a second time after one or two extra precipitations.

Final samples of 2-chlorobenzalacetophenone copolymers were white, fibrous and fairly

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[3] Analyses were carried out by J. Nemeth, E. L. Fett, and L. Chang.

[4] In one or two cases it was necessary to allow suspensions to settle overnight.

tough. The ester copolymers were softer, especially those having lower ester incorporation; some were very sticky.

Procedure for emulsion runs. Emulsion reactions were run in four-ounce, screw-cap bottles sealed with rubber gaskets. Bottles were charged with non-volatile ingredients first; then after cooling in an ice-bath, the required amounts of liquid butadiene were poured in. After removing from the ice-bath and allowing the butadiene to boil briefly to force out the air, the bottles were sealed. (Weights of monomers were determined by differential weighings of the bottles.) Bottles then were oscillated in a constant temperature bath 80 times per minute for the required time as determined by trial runs. After cooling, bottles were opened and the products were coagulated with 30-ml. portions of salt-acid coagulant (787.5 g. of NaCl, 53.3 g. of H_2SO_4, and 2250 ml. of H_2O). The products then were separated from the coagulant either by decantation or by extraction with benzene depending upon the consistency of the mixture. In either case benzene solutions of the mixtures were filtered (very slowly) through number 1 paper into five-fold volumes of stirred methanol containing about 0.1 g. of hydroquinone. After decanting, the yields were dried and weighed. Reprecipitation and preparation for analysis were carried out in the same way as described above for the bulk runs except that the benzene solutions were filtered between each precipitation as well as at the end to make sure that no inorganic material remained suspended in the benzene to be carried along into the final product.

Homopolymerization of methyl 4-chlorocinnamate. Methyl 4-chlorocinnamate (13.65 g.) was heated with a small amount of benzoyl peroxide (0.035 g.) at 100–110° in a sealed glass tube. After the first few hours an appreciable quantity of gelatinous solid separated from the liquid. After seven days the mixture was stirred into 300 ml. of boiling methanol and filtered while hot. The solid retained by the filter dissolved almost completely when stirred with 40 ml. of chloroform. The solution was passed through a 200 mesh screen to remove a small amount of undissolved gel, and the polymer was precipitated in a four-fold volume of methanol. It was separated from the liquid by centrifugation and dried in a vacuum desiccator overnight. When dry the polymer was a brittle, amorphous, white solid which darkened when heated to 340–355° in a melting point tube. The yield was only 2.5 per cent. An analytical sample was prepared by one further reprecipitation from chloroform into methanol.

Anal. Calc'd for $(C_{10}H_9ClO_2)_n$: C, 61.06; H, 4.61; Cl, 18.04.
Found: C, 60.77; H, 4.68; Cl, 18.25.

Attempted homopolymerization of methyl 2-chlorocinnamate. Methyl 2-chlorocinnamate, 19.87 g., was heated with benzoyl peroxide (0.050 g.) in a sealed tube for seven days exactly as described above for the 4-chloro ester. During this time the only observed change was an almost imperceptible darkening. When the contents were poured into methanol, no trace of precipitate appeared.

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SUMMARY

Reactivity ratios for butadiene and 2-chlorobenzalacetophenone copolymerized in bulk at 60° have been found to equal (r_1) 0.78 ± 0.12 and (r_2) −0.02 ± 0.05. In an emulsion recipe these values were found to be virtually unchanged. Butadiene and methyl 2-chlorocinnamate showed values of 1.07 ± 0.12 for r_1 and

-0.02 ± 0.05 for r_2 in bulk at 60°; at 80° values of 1.20 ± 0.12 for r_1 and -0.03 ± 0.05 for r_2 were obtained. Efforts to purify butadiene methyl 4-chlorocinnamate copolymers failed; but using an estimate of impurity content obtained by extrapolation, values of 2.7 ± 0.3 for r_1 and 0.00 ± 0.05 for r_2 (in bulk at 80°) were determined. Methyl 4-chlorocinnamate (but not methyl 2-chlorocinnamate) has been homopolymerized at 100–110°.

Relationships between reactivity ratios and structure are discussed.

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