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Copolymerization. X. The Effect of *meta*- and *para*-Substitution on the Reactivity of the Styrene Double Bond

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Although previous work has established the validity of the copolymerization equation² as a description of the free radical copolymerization of a large number of systems,³ interpretation of the monomer reactivity ratios observed has been neither simple nor unequivocal. Thus, the reactivities of monomers in copolymerization depend both upon a general order of reactivity, apparently independent of the attacking radical and related to the resonance stabilization of the radical resulting from reaction, and a specific tendency of certain monomers to alternate in copolymerization. This "alternating tendency" has proved to be of particular interest, and polar interaction,^{4,5} electron donor-acceptor properties⁶ and actual compound formation,⁴ have been suggested as possible causes. Still further factors appear to be involved in the interpretation of the relative reactivities of *cis-trans* isomers,⁷ and in some systems, where monomer reactivity ratios appear to depend upon differences in both heats and entropies of activation⁸ the situation is still further complicated.

Since any attempt to identify or evaluate all of these factors in the copolymerization of the usual monomers appeared to us a formidable undertaking, we have looked for a simpler system. We have chosen the *meta* and *para*-substituted styrenes since the effect of *meta* and *para* substitution on the rates and equilibria of (polar) side-chain reactions of benzene appear to be particularly simple and well understood. Thus, Hammett, who has surveyed available data on a wide variety of such side-chain reactions of benzene,⁹ has found that, in general, the effect of *meta*- or *para*-substituents can be expressed by the relation $\log K_0/K = \sigma\rho$, where K_0 and K are the rate or equilibrium constants for the reaction of the unsubstituted and substituted compound, σ a parameter having a single value for each substituent and ρ a constant for any particular reaction. The parameters σ and ρ are probably best inter-

preted as measures, respectively, of the ability of the substituent to withdraw electrons or make them available at the site of reaction and the effect of such electron-availability on the reaction considered.

If a given monomer (M_1) is copolymerized in turn with a series of substituted styrenes (M_2 's), the reciprocals of the monomer reactivity ratios for the radical corresponding to that monomer ($1/r_1$'s) are the relative reactivities of the substituted styrenes with that radical. Such series, obtained with several radicals, might permit the assigning of a value to each substituent analogous to Hammett's σ value, but applying now to radical reactions rather than to ones proceeding through "polar" intermediates. In particular, it was hoped that such a series might throw light on the nature and magnitude of the "alternating effect" in copolymerization.

Experimental

Materials.—Styrene and methyl methacrylate were commercial materials, distilled before use and stored in the ice-box. *p*-Methoxy, *p*-chloro, *m*-chloro, *o*-chloro- and *m*-bromostyrene were prepared by the decarboxylation of the corresponding cinnamic acids. Their preparation and properties are described elsewhere,¹⁰ as are the preparation and properties of the samples of *p*-iodo, *p*-nitro and *p*-dimethylaminostyrene.¹¹ *p*-Bromostyrene was prepared by the aluminum isopropoxide reduction of *p*-bromoacetophenone followed by dehydration over potassium bisulfate essentially as described by Brooks.¹² An over-all yield of 32.8% of product was obtained, b. p. 49.5–50.0° (2.5 mm.), n_D^{20} 1.5952 (lit. gives b. p. 83.5–84.5 (11 mm.), n_D^{20} 1.5961).¹³ By similar procedures were prepared *p*-methylstyrene in over-all yield of 34.7%, b. p. 59.3–59.5° (15.5 mm.), n_D^{20} 1.5425 (lit. gives b. p. 65–66 (18 mm.), n_D^{20} 1.5402¹⁴), and *p*-cyanostyrene in over-all yield of 15.2%, b. p. 69–71 (2 mm.), n_D^{20} 1.5795 (lit. gives b. p. 102–4 (9 mm.), n_D^{20} 1.5781¹⁵). *m*-Methylstyrene was a sample supplied by Dr. Schoene of the Naugatuck Chemical Co. Refractionation here, it had an index of refraction n_D^{20} of 1.5402 (lit. n_D^{20} 1.5410¹⁶).

Copolymerization Technique.—Polymerizations were carried out at 60° in sealed evacuated tubes essentially as described in the first paper in this series,^{2b} using 0.05 to 0.10 mole total monomers and 0.1 mole % benzoyl peroxide in each experiment. In general two experiments each at 1:4 and 4:1 molar ratios were carried out on each

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(2) (a) Alfrey and Goldfinger, *J. Chem. Phys.*, **12**, 205 (1944);

(b) Mayo and Lewis, *THIS JOURNAL*, **66**, 1594 (1944); Wall, *ibid.*, 2050.

(3) For a recent summary and references, see Mayo, Lewis and Walling, *ibid.*, **70**, 1529 (1948).

(4) Mayo, Lewis and Hulse, *THIS JOURNAL*, **67**, 1701 (1945).

(5) (a) Price, *J. Polymer Sci.*, **1**, 83 (1946); (b) Alfrey and Price, *ibid.*, **2**, 101 (1947).

(6) Bartlett and Nozaki, *THIS JOURNAL*, **68**, 1495 (1946).

(7) Lewis and Mayo, *ibid.*, **70**, 1533 (1948).

(8) Lewis, Walling, Cummings, Briggs and Mayo, *ibid.*, **70**, 1519 (1948).

(9) Hammett "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, Ch. VII.

(10) Walling and Wolfstirn, *THIS JOURNAL*, **69**, 852 (1947).

(11) Strassburg, Gregg and Walling, *ibid.*, **66**, 2141 (1947). The authors are also indebted to Mr. Strassburg for the preparation of the styrenes described below.

(12) Brooks, *ibid.*, **66**, 1295 (1944).

(13) Ziegler and Tiemann, *Ber.*, **55**, 3414 (1922).

(14) Mowry, Renoll and Huber, *THIS JOURNAL*, **68**, 1105 (1946).

(15) Marvel and Overberger, *ibid.*, **67**, 2250 (1945).

(16) Marvel, Overberger, Allen and Saunders, *ibid.*, **68**, 736 (1946). The sample from Dr. Schoene was obtained by the steam distillation of unreacted monomers from a butadiene-*m*-methylstyrene copolymer and is believed to have come originally from the University of Illinois.

Experiments on Complexes.—Absorption coefficients for violet light for maleic anhydride-substituted styrene complexes were measured using a Cenco photometer with a Corning #511 filter. Chloroform solutions giving 30–70% transmission (approximately 3 molar in styrene and 2 molar in maleic anhydride for most of the styrenes) were employed and $\log_{10} I_0/I$ calculated for a solution 1 molar in each component, assuming a highly dissociated 1:1 complex following the law $\log I_0/I = K [\text{styrene}][\text{maleic anhydride}]$. The high dissociation and obedience to the above law was established for styrene–maleic anhydride

TABLE II

MONOMER REACTIVITY RATIOS AND DERIVED QUANTITIES FOR THE COPOLYMERIZATION OF STYRENE (M_1) WITH SUBSTITUTED STYRENES (M_2)

Substituent	Assumed ^a error, %	r_1	r_2	$r_1 r_2$	Log rel. reactivity ^b	Hammett σ value
<i>p</i> -OCH ₃	0.1 C ^a	1.16 \pm 0.09	0.82 \pm 0.07	0.95 \pm 0.11	-0.065 \pm 0.034	-0.268
<i>p</i> -N(CH ₃) ₂	.1 N	1.015 \pm .06	0.84 \pm .05	0.85 \pm .07	-.006 \pm .027	-.205
None	1.00	1.00	1.00	.000	.000
<i>p</i> -Cl	.1 Cl	0.74 \pm .03	1.025 \pm .05	0.76 \pm .05	.132 \pm .018	.227
<i>p</i> -Br	.2 Br	.695 \pm .02	0.99 \pm .07	.69 \pm .05	.158 \pm .013	.232
<i>p</i> -I	.5 I	.62 \pm .05	1.25 \pm .30	.76 \pm .20	.208 \pm .035	.276
<i>m</i> -Cl	Std. dev. ^c	.64 \pm .05	1.09 \pm .23	.70 \pm .16	.193 \pm .034	.373
<i>m</i> -Br	Std. dev. ^c	.55 \pm .03	1.05 \pm .21	.58 \pm .13	.260 \pm .024	.391
<i>p</i> -CN	0.1 N	.28 \pm .025	1.16 \pm .13	.325 \pm .047	.553 \pm .039	1.000 ^d
<i>p</i> -NO ₂	.1 N	.19 \pm .02	1.15 \pm .20	.218 \pm .045	.722 \pm .046	1.27 ^d

^a Analytical error assumed in calculating errors in subsequent columns. ^b *I. e.*, $-\log_{10} r_1$. ^c See text. ^d Value for reaction with phenols and amines (the only one available for *p*-CN). ^e Small experimental error achieved through use of simultaneous blanks in analysis. Unusual accuracy was required in this case because of small difference in carbon analysis between monomers.

TABLE III

MONOMER REACTIVITY RATIOS AND DERIVED QUANTITIES FOR THE COPOLYMERIZATION OF METHYL METHACRYLATE (M_1) WITH SUBSTITUTED STYRENES (M_2)

Substituent	Assumed ^a error, %	r_1	r_2	$r_1 r_2$	Log rel. reactivity ^b	Hammett σ value
<i>p</i> -OCH ₃	0.1 C	0.29 \pm 0.03	0.32 \pm 0.05	0.093 \pm 0.017	0.230 \pm 0.045	-0.268
<i>p</i> -N(CH ₃) ₂	.1 N	.205 \pm .02	.11 \pm .02	.023 \pm .005	.351 \pm .042	-.205
<i>p</i> -CH ₃	.2 C	.405 \pm .025	.44 \pm .02	.178 \pm .014	.056 \pm .027	-.170
<i>m</i> -CH ₃	.2 C	.53 \pm .025	.49 \pm .02	.26 \pm .02	-.062 \pm .021	-.069
None ^f	.2 C	.46 \pm .026	.52 \pm .026	.24 \pm .02	.000	.000
<i>p</i> -Cl	.1 Cl	.415 \pm .02	.89 \pm .05	.37 \pm .03	.046 \pm .021	.227
<i>p</i> -Br	.2 Br	.395 \pm .02	1.10 \pm .25	.44 \pm .10	.067 \pm .022	.232
<i>p</i> -I	.5 I	.36 \pm .03	0.95 \pm .20	.34 \pm .08	.107 \pm .036	.276
<i>m</i> -Cl	Std. dev. ^c	.47 \pm .075	0.91 \pm .11	.43 \pm .09	-.009 \pm .070	.373
<i>m</i> -Br	0.2 Br	.48 \pm .02	1.17 \pm .25	.56 \pm .12	-.018 \pm .018	.391
<i>p</i> -CN	0.1 N	.22 \pm .02	1.41 \pm .13	.31 \pm .04	.321 \pm .040	1.000 ^d

^f From data of ref. (2b) recalculated in ref. (8). ^g Compared with styrene, *i. e.*, $\log 0.46 - \log r_1$. Other footnotes have same significance as in Table II.

TABLE IV

MONOMER REACTIVITY RATIOS FOR COPOLYMERIZATIONS OF SOME ADDITIONAL VINYL AROMATICS

M_1	M_2	Assumed error	r_1	r_2
<i>p</i> -Chloro- styrene	<i>p</i> -Methyl- styrene	0.1% Cl	1.15 \pm 0.05	0.61 \pm 0.03
<i>p</i> -Chloro- styrene	<i>p</i> -Methoxy- styrene	0.1% Cl	0.86 \pm .08	.58 \pm .03
<i>p</i> -Chloro- styrene	<i>p</i> -Nitro- styrene	Std. dev.	0.70 \pm .08	.91 \pm .37

by Dr. F. M. Lewis in another study in this Laboratory.

Complexes with chloranil were much more stable and showed appreciable color in concentrations ranging from 0.008 *M* chloranil in 0.35 *M* styrene for the styrene-chloranil complex to 0.000003 *M* chloranil in 0.05 *M* *p*-dimethylaminostyrene for the *p*-dimethylaminostyrene complex.

Trinitrobenzene complexes were prepared by dissolving 1,3,5-trinitrobenzene in the styrenes and appeared to show intermediate intensity of color.

Results and Discussion

Relative Reactivities toward Styrene-type Radicals.—Monomer reactivity ratios and some

derived quantities for the copolymerizations described in Table I are listed in Table II. In Figure 2 the logarithms of the relative reactivities of the substituted styrenes toward the unsubstituted styrene radical are plotted against Ham-

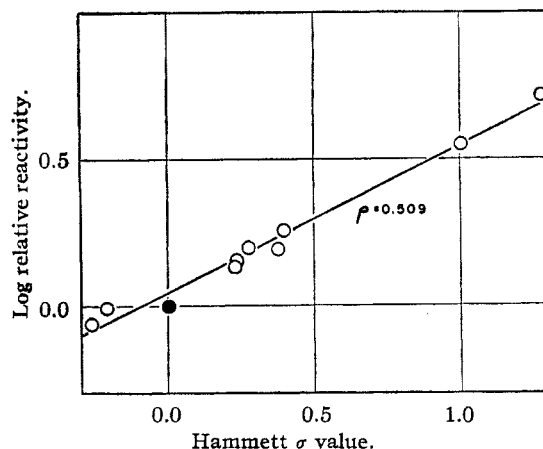


Fig. 2.—Plot of log relative reactivity toward the styrene type radical vs. Hammett σ value of substituent for various substituted styrenes.

mett's σ values for the same substituents. Strikingly, excellent correspondence is observed between the relative reactivities and Hammett's σ values. The median deviation of points from the best straight line (drawn by the method of least squares) is only 0.024 log unit, less than the average experimental error, and better than all but six of the 52 polar reactions originally investigated by Hammett.⁹ In short, this radical reaction behaves like an ordinary polar reaction with a ρ value (the slope of the line in Fig. 1) of 0.509, approximately the same as that for the ionization of phenylacetic acids.^{9,18}

If the Hammett σ values may be interpreted as measures of electron density at the site of reaction (here the substituted styrene double bond) this result suggests that polar interaction between reactants, perhaps of the sort suggested by Price and Alfrey,⁵ may be of primary importance in determining reactivity in this series. Further, since ρ is positive and dipole measurements¹⁹ show the styrene double bond to possess an absolute negative charge, the styrene-type radical must possess an effective negative charge as well as it approaches the monomer.²⁰

If such a polar interaction were here the primary

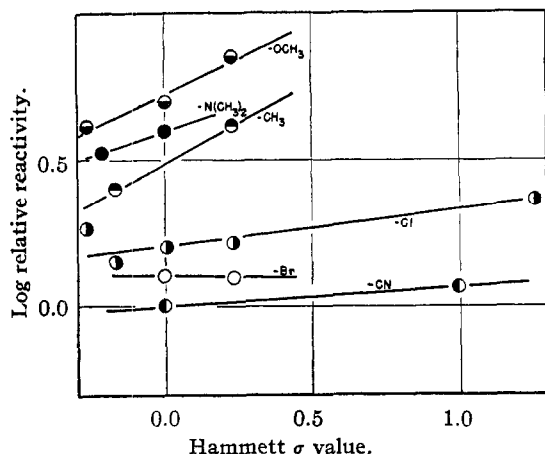
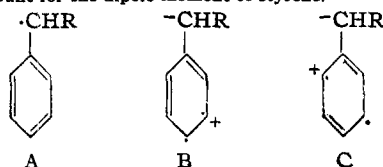


Fig. 3.—Plot of log relative reactivities toward indicated *para*-substituted styrene radicals vs. Hammett σ values for various substituted styrenes. Height of ordinate scale is arbitrary.

(18) Kindler, *Ann.*, **452**, 90 (1927).

(19) Styrene has a dipole moment of 0.37 debye unit, opposite in direction to toluene, Otto and Wenzke, *THIS JOURNAL*, **57**, 294 (1935).

(20) Since both reactants would possess like charges, this could hardly represent an induced polarization, but must correspond to either a general inductive effect of the ring or contributions from structures such as B and C, similar to those which might be called upon to account for the dipole moment of styrene.¹⁹



factor in determining relative reactivity, it would be predicted that substituting the styrene radical with negative (electron-attracting) groups should decrease the magnitude and possibly even change the sign of its charge. As a result, the reactions of styrenes with negatively substituted styrene radicals should have decreasing and perhaps even negative ρ values. In Fig. 3 are plotted relative reactivities taken from the more reliable data of Tables II and IV vs. σ values for the reactions of some substituted styrene radicals with substituted styrenes. Although the prediction is realized, the ρ values seem to fall into two sharp classes, positive and roughly equal for styrene and positively substituted styrenes, and close to zero for those with negative substituents.

The interpretation given above fails to take into account any contribution from the differing resonance stabilizations of the resulting substituted styrene radicals to the reactivities of the substituted styrenes.^{3,4,5,21} On the other hand, if the results illustrated in Fig. 3 are to be ascribed entirely to such differential stabilization, the close agreement with the Hammett series must be partly coincidental, and the decreased reactivities of the *p*-methoxy- and *p*-dimethylaminostyrenes (for which plausible additional resonance forms can be drawn) are surprising. Furthermore, there then seems to be no simple way of accounting for the observed reactivities toward substituted styrene radicals (*cf.* Fig. 3).

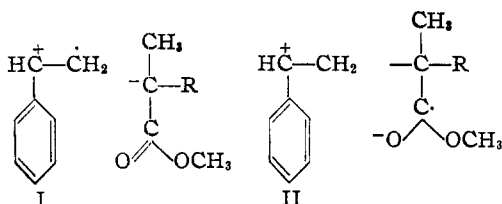
That resonance stabilization of the resulting radicals may, however, play some role in the observed reactivities is suggested by a closer inspection of Fig. 2, where it will be noted that the (black) point corresponding to styrene lies appreciably below the best square line. Since all other points were determined by comparison with styrene, purely random scatter would be expected to put the styrene point on the line. On the other hand, such a result may be due to increased reactivity of all the substituted styrenes due to additional resonance stabilization of their resulting radicals above that arising from polar interaction. It is likely that both factors are involved to some degree, but a determination of their relative magnitudes is not as yet possible.

Relative Reactivities toward the Methyl Methacrylate Radical.—Monomer reactivity ratios for the reaction of methyl methacrylate with eleven substituted styrenes are listed in Table III, and, in Fig. 4, logarithms of relative reactivities are plotted against the Hammett σ values for the substituents. It can be immediately seen that, unlike the case for reaction with the styrene radical, no simple linear relation is evident and no generally applicable value of ρ can be selected. In short, in the case of this radical, derived from the class of carbonyl-conjugated monomers which tend to alternate in copolymerization with sty-

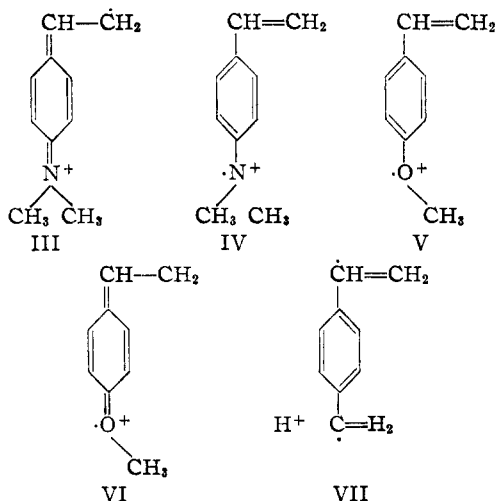
(21) Wheland, "The Theory of Resonance," John Wiley and Sons, Inc., New York, N. Y., 1944, Chap. 8.

rene,^{2b,3} some additional factor besides those considered in the preceding section must be at work determining the effect of substituents on reactivity.

Other cases of deviation from the usual Hammett series can sometimes be accounted for by special resonance forms available to one of the reactants in the transition state.²² Here, since the respective electron accepting and donating properties of carbonyl-conjugated and aromatic systems are well recognized, it seems reasonable to consider the possible contributions of non-bonded and bonded structures such as I and II.²³ Since trans-



fer of an electron to give the non-bonded structure I transforms the methacrylate radical to the relatively stable enolate ion, while the styrene radical carbonium ion may resonate through some twenty-six more or less equivalent forms, structure I appears to have considerable plausibility. Similarly, the energy difference gained in forming a C-C bond while opening a carbonyl group and by the shifting of a negative charge to oxygen suggests that contributions from II might also be important. Inspection of Fig. 4, however, indicates that the chief problem in this discussion lies in



(22) Thus, for example, the necessity of assigning two σ values to the *p*-nitro group, one for the reactions of amines and phenols, in all probability arises from the heightened resonance possibilities between nitro and $-\text{OH}$ or $-\text{NH}_2$ groups. Physical evidence of such interaction has long been available from dipole moments, increased color, etc.

(23) The possibility of the importance of special resonance structures in the transition state as a means of interpreting alternation in copolymerization was first made to us by Prof. Saul Winstein of the University of California at Los Angeles, and we are indebted to him for several discussions which have been most helpful in formulating the viewpoint expressed here.

accounting for the high reactivities of *p*-dimethylamino-, *p*-methoxy- and, to a lesser degree, *p*-methylstyrene. By this interpretation, there should be available to them additional forms not possessed by the styrene radical carbonium ion. A number of such structures can be drawn, of which III-VII are examples.

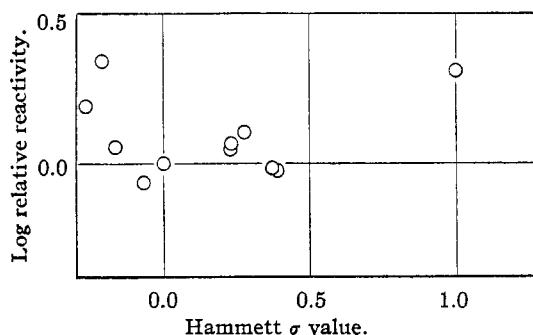
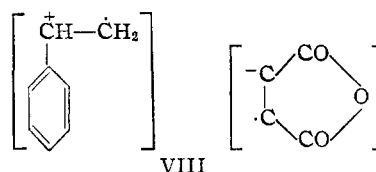


Fig. 4.—Plot of log relative reactivity toward the methyl methacrylate type radical vs. Hammett σ value of substituent for various substituted styrenes.

An interesting property of unsaturated carbonyl compounds and similar materials (maleic anhydride, quinones, polynitrobenzenes, etc.) is that they form colored molecular complexes with styrenes and other aromatic compounds. A suggested structure of these materials is one consisting of pairs of radical ions in which the aromatic compound has donated an electron to the conjugated carbonyl system,²⁴ for styrene-maleic anhydride, the hybrid resulting from the resonance between various forms of VIII.



Inspection of VIII shows the styrene portion to be identical with I. It is thus evident that, if the unbonded resonance forms are important, a relation should exist between the complex forming tendency of substituted styrenes and their tendency to copolymerize with acceptor radicals.²⁵ Some observations on such complexes are listed in Table V in which the nature of light absorption of complexes of substituted styrenes with maleic anhydride, 1,3,5-trinitrobenzene, and chloranil is compared with their reactivity toward the methacrylate radical. Maleic anhydride yields rather unstable complexes, highly dissociated in solution and, since all are yellow in dilute solution, their relative absorption of violet light has been com-

(24) Weiss, *J. Chem. Soc.*, 245 (1942).

(25) A relation between the complex forming and copolymerizing tendencies of maleic anhydride has been suggested by Bartlett and Nozaki, ref. 6. Also Woodward, *THIS JOURNAL*, 64, 3058 (1942), has postulated the existence of structures similar to VIII in the transition state of the Diels-Alder reaction.

pared. Chloranil complexes are more stable (preliminary measurements indicate dissociation constants of 1–5 and heats of dissociation of 0 to –1500 cal./mole) and have absorption maxima in the visible spectrum, while trinitrobenzene complexes have intermediate properties. Examination of the data of Table V shows a very reasonable correlation between increasing depth of color (shade or intensity) and reactivity, and lends strong support, in general, to the idea of a relation between the complex forming tendency of styrenes and their ease of copolymerization with radicals conjugated with a carbonyl system, and in particular, to the idea of the importance of special forms in the transition state of such copolymerizations.

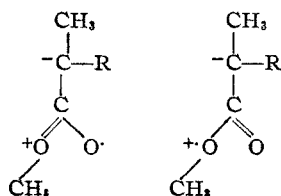
TABLE V
COMPLEXES OF SUBSTITUTED STYRENES

Sub- stituent	Rel. react- ivity	Maleic color	anhydride inten- sity ^a	Trinitro- benzene color	Chloranil color
<i>p</i> -OCH ₃	1.59	Yellow	3.95	Orange	Red-violet
<i>p</i> -N(CH ₃) ₂	2.24	Red ^b	20.5	Deep violet	Sky blue
<i>p</i> -CH ₃	1.14	Yellow	0.202	Deep yellow	Orange
<i>m</i> -CH ₃	0.87	Yellow	.080	Yellow
None	1.00	Yellow	.027	Yellow	Yellow
<i>p</i> -Cl	1.11	Yellow	.046	Yellow	Yellow
<i>m</i> -Cl	0.98	Yellow	.019	Pale yellow

^a Log I_0/I for a 10-mm. cell containing 1 *M* styrene and 1 *M* maleic anhydride in chloroform viewed with a Corning 511 (violet) filter. ^b Yellow in dilute solution.

Even though special resonance forms are of primary importance in determining the reactivities of styrenes toward the methacrylate radical, some contribution might still be expected from the resonance structures of the resulting radical and (unless the methacrylate radical is just electrically neutral) polar interactions. Some evidence for such contribution is gained from Fig. 4, for, if the points for *p*-methyl-, *p*-dimethylamino-, and *p*-methoxystyrenes (the monomers showing the highest complex-forming tendencies) are omitted, a line can be drawn through the remaining points corresponding to a ρ value of 0.33 with the reasonable median deviation of 0.04 log unit. Differences in reactivities of these styrenes may thus be due to the same factors as govern reactivity toward the styrene radical.²⁶ Consideration of these factors also aids in interpreting the r_2 values

(26) The same difficulties arise, however, in assessing the importance of differences in the resonance stabilization of the resulting radical. If such differences are minor, incidentally, and the effects primarily polar, we are led to the conclusion that the methacrylate radical possesses a partial negative charge. Since the ester group would usually be expected to attract rather than donate electrons, this conclusion is surprising and suggests the possibility of resonance forms such as



in Table III. Thus, negatively substituted styrene radicals show little preference in reaction with their own monomers or methacrylate, paralleling their behavior toward styrene. On the other hand, the styrene radicals with electron-supplying groups show heightened reactivity toward methacrylate, as might be anticipated since structures analogous to I–VII can be drawn in which an electron has been donated from the styrene radical to the methacrylate double bond.

The necessity of considering special resonance forms related to those involved in molecular complex formation in interpreting the copolymerization of styrenes with even such a weakly alternating monomer as methyl methacrylate ($r_1r_2 = 0.24$) makes it appear likely that they, rather than some sort of simple electrostatic interaction, are primarily responsible for the “alternating effect” in copolymerization. Accordingly, it seems doubtful to us that the equation of Alfrey and Price²⁷ has any real theoretical justification.²⁷ The determination of the relative reactivities of styrenes with a more strongly electron accepting radical is described in Paper XII of this series, and will be the subject of future communications.

Summary

1. Copolymerizations of methyl methacrylate and styrene with eleven *meta* and *para* substituted styrenes have been carried out and the monomer reactivity ratios calculated.

2. The relative reactivities of the substituted styrene radical closely follow the order found by Hammett for “polar” side-chain reactions of benzene, with a ρ value of 0.509. Negatively substituted styrene radicals show lower ρ values. These results are interpreted as being due to the effect of substituents on the polar interaction between the styrene and the radical as they approach the transition state and on the resonance stabilization of the resulting radicals.

3. Relative reactivities of substituted styrenes toward the methyl methacrylate type radical fail to follow a Hammett series. These results are interpreted as being due to the effect of contributions of non-bonded resonance forms to the transition state in which the radical has accepted an electron, superimposed upon factors similar to those involved in reaction with the styrene radical.

4. Molecular complexes between substituted styrenes and maleic anhydride, trinitrobenzene and chloranil have been investigated and a relation between complex forming tendency and abnormal reactivity toward the methacrylate radical noted and interpreted on the basis of the importance of non-bonded resonance structures.

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(27) Attempts to calculate Q 's and e 's by Alfrey and Price's equation for the systems reported here have not given very satisfactory agreement with experiment and have fallen down particularly in the cases where strong alternation occurs.