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Ionic Polymerization. II. Copolymerization of Styrene, *p*-Chlorostyrene and α-Methylstyrene with Meta and Para Substituted Styrenes Catalyzed by Stannic Chloride[1,2]

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RECEIVED NOVEMBER 21, 1951

A study of the cationic-catalyzed copolymerization of vinyl monomers should be an effective way of obtaining relative reactivities of monomers toward carbonium ions. In particular, it was of interest to know whether the copolymerization of meta and para substituted styrenes with styrene, *p*-chlorostyrene and α-methylstyrene as reference monomers would give information which could be correlated with the σ-constants of Hammett. In addition, it was anticipated that such information would contribute to an understanding of the detailed mechanism of cationic-catalyzed polymerization and give some indication as to the effect of the anion on the reactivity of a carbonium ion in an ion pair. Reactivity ratios were determined for the copolymerization of styrene with *p*-nitro-, *p*-methoxy-, *m*-nitro-, *m*-methoxy- and *m*-chlorostyrenes catalyzed by stannic chloride. The effect of reaction conditions such as catalyst concentration and dielectric constant for such a system on the monomer reactivity ratios had previously been shown to be negligible. A plot of log $1/r_1$ *vs.* σ is given. Deviations in the case of *p*- and *m*-methoxystyrenes are discussed. No appreciable copolymerization occurs with *p*-nitrostyrene. In a like manner, reactivity ratios were determined for the copolymerization of *p*-chlorostyrene with *p*-bromo-, *p*-methyl- and *m*-methoxystyrenes. Again a plot of log $1/r_1$ *vs.* σ gives a straight line with the exception of *m*-methoxystyrene which shows enhanced reactivity. Data and similar curves for the copolymerization of α-methylstyrene with *p*-dimethylamino-, *p*-methoxy- and *m*-methoxystyrenes are also presented. Assuming that the propagation step in carbonium ion polymerization involves the reaction of an ion pair with a monomer, it would appear that the monomer reactivities approximate Hammett's sigma series except for the *m*- and *p*-methoxy and *p*-dimethylamino substituted monomers. Explanations for the reported deviations are discussed.

A study of the cationic-catalyzed copolymerization of vinyl monomers should be an effective way of obtaining relative reactivities of monomers toward carbonium ions. It seems particularly applicable to use as a method of determining or detecting the effect of the anion of the ion pair on the reactivity of carbonium ions.

In an earlier paper, a study of the effect of reaction conditions on the reactivity ratios was made for the system styrene–*p*-chlorostyrene catalyzed by stannic chloride. The results of this investigation demonstrated that in the system studied with stannic chloride as a catalyst, the effect of the dielectric constant of the reaction medium on the reactivity ratios was small.[4] This fact supported the idea that relative reactivities of carbonium ions derived from substituted styrenes could be determined with the aid of the copolymerization technique. In particular, we were interested in knowing whether the copolymerization of meta and para substituted styrenes with styrene, *p*-chlorostyrene and α-methylstyrene would give information which could be correlated with the σ-constants of Hammett.[5]

Experimental

Monomers.—The source and purification of *p*-chlorostyrene, α-methylstyrene and styrene were reported in the previous paper.[1]

p-Methoxystyrene was prepared according to the procedure of Quelet[6a] as modified by Frank, Adams, Allen, Gander and Smith,[6b] b.p. 85° (12 mm.), $n^{24}\mathrm{D}$ 1.5590 (b.p. 94° (17 mm.), $n^{15}\mathrm{D}$ 1.5640).[6a]

p-Dimethylaminostyrene was prepared according to the procedure of Marvel, Overberger, Allen and Saunders[7a] and Strassburg, Gregg and Walling,[7b] m.p. 15–16°, $n^{24.5}\mathrm{D}$ 1.6000 (16.5°, $n^{20}\mathrm{D}$ 1.6121)[7b] ($n^{20}\mathrm{D}$ 1.6010).[7a]

p-Nitrostyrene was obtained from Monomer–Polymer Incorporated. The monomer was purified by addition to methanol to remove polymer and crystallized at −40° from methanol as recommended by reference 7b, m.p. 20.5–21° (21.4°).

p-Bromostyrene was prepared from *p*-bromobenzaldehyde according to the procedure described for *p*-chlorostyrene.[1,9] The pure monomer was obtained by fractional distillation through a helices-packed column, b.p. 52–53° (2 mm.), $n^{25}\mathrm{D}$ 1.5893 ($n^{18}\mathrm{D}$ 1.5940),[8a] ($n^{18}\mathrm{D}$ 1.5990).[8b]

p-Methylstyrene was prepared from *p*-bromotoluene according to the procedure described for the preparation of *m*-chlorostyrene in reference 9. From 307.8 g. (1.8 moles) of *p*-bromotoluene, 43.7 g. (1.8 moles) of magnesium turnings and 90 g. (2.05 moles) of acetaldehyde, there was obtained 170.8 g. (69.7%) of *p*-methylphenylmethylcarbinol, $n^{24}\mathrm{D}$ 1.5238, b.p. 110° (10 mm.) ($n^{25}\mathrm{D}$ 1.5203, prepared from *p*-tolyl methyl ketone by catalytic reduction).[10] From 170.8 g. (1.255 moles) of carbinol, there was obtained 104.8 g., 70.5% of *p*-methylstyrene, $n^{25}\mathrm{D}$ 1.5395, b.p. 82–83° (27 mm.) ($n^{25}\mathrm{D}$ 1.5402, prepared by catalytic dehydration over alumina).[10]

m-Chlorostyrene was prepared according to the directions described by reference 9.

m-Methylstyrene was prepared by a similar procedure by the addition of acetaldehyde to the Grignard reagent from *m*-bromotoluene and dehydration of the carbinol, b.p. 49–52° (3 mm.), $n^{19}\mathrm{D}$ 1.5406 (b.p. 50–51° (3 mm.), $n^{20}\mathrm{D}$ 1.5410).[7a]

m-Nitrostyrene was prepared according to the procedure of reference 7a, b.p. 98–101° (3 mm.), $n^{19.5}\mathrm{D}$ 1.5824 (b.p. 96–100° (3 mm.), $n^{20}\mathrm{D}$ 1.5830).[7a] It was also prepared

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[1] This is the second in a series of papers concerned with the methods and mechanism of ionic polymerization. For the first paper in this series, see C. G. Overberger, Lester H. Arond and John J. Taylor, THIS JOURNAL, **73**, 5541 (1951). Please note that Lester H. Arond was misspelled in the previous paper.

[2] A portion of this work was supported by a contract from the Office of Naval Research.

[3] A portion of a thesis by Lester H. Arond submitted to the Polytechnic Institute of Brooklyni n partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[4] Florin has demonstrated that a change in the reactivity ratios in the copolymerization of *o*-chlorostyrene and styrene with the dielectric constant occurs with aluminum chloride as the catalyst. He likewise finds no significant change, however, with stannic chloride as the catalyst. See also R. E. Florin, THIS JOURNAL, **73**, 4468 (1951).

[5] L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, p. 184.

[6] (a) R. Quelet, *Bull. soc. chim.*, **7**, 196 (1940); (b) R. L. Frank, C. E. Adams, R. E. Allen, R. Gander and P. V. Smith, THIS JOURNAL, **68**, 1365 (1946).

[7] (a) C. S. Marvel, C. G. Overberger, R. E. Allen and J. H. Saunders, *ibid.*, **68**, 736 (1946); (b) R. W. Strassburg, R. A. Gregg and C. Walling, *ibid.*, **69**, 2141 (1947).

[8] (a) D. Sontag, *Ann. chim.*, [11] **1**, 359 (1934); (b) R. Quelet, *Bull. soc. chim.*, [4] **45**, 75 (1929).

[9] C. G. Overberger and J. H. Saunders, *Org. Syntheses*, **28**, 31 (1948).

[10] D. T. Mowry, M. Renoll and W. F. Huber, THIS JOURNAL, **68**, 1105 (1946).

from *m*-nitrocinnamic acid according to the procedure of Wiley and Smith, b.p. 105–107° (6 mm.), n^{24}D 1.5828 (96° (3.5 mm.), n^{20}D 1.5830).[11]

m-Methoxystyrene was prepared according to the general procedure of Frank, Adams, Allen, Gander and Smith[6b] from *m*-bromoanisole, n^{20}D 1.5541 (n^{20}D 1.5540).[6b] *m*-Bromophenol was prepared from *m*-bromoaniline according to the directions described in reference 12 for the preparation of 3-bromo-4-hydroxytoluene and Natelson and Gottfried.[13] This latter procedure which uses hydrochloric acid instead of sulfuric in the diazotization step, and a shorter reaction time gave better yields. *m*-Bromoanisole was prepared according to the directions of the latter investigators. β-(*m*-Methoxyphenyl)-ethyl alcohol was prepared from *m*-bromoanisole according to the directions of Natelson and Gottfried. From 120 g. (0.641 mole) of *m*-bromoanisole, 17 g. of magnesium (0.69 g. atom) and 35 g. (0.795 mole) of ethylene oxide there was obtained 49 g. (50%) of β-(*m*-methoxyphenyl)-ethyl alcohol, b.p. 150° (14 mm.), n^{21}D 1.5390 (n^{20}D 1.5390).[6b]

TABLE I

COPOLYMERIZATION OF STYRENE WITH SUBSTITUTED STYRENES[a]

M_2 in monomer mixture[b]	Reaction time, hr.	Conversion, %	N.[d] %		m_2
Styrene (M_1) and *m*-Nitrostyrene (M_2)[c]					
0.198	1.3	6.0	0.22		0.016
.298	1.4	5.5	.31		.023
.407	1.7	5.9	.42		.031
.497	2.4	5.5	.50		.038
.595	3.3	4.5	.87		.066
.745	26.1	4.4	1.17		.091
Styrene (M_1) and *m*-Methoxystyrene (M_2)[c]					
			C.[e] %	H.[e] %	
0.191	2.5	5	89.0	7.74	0.226
.323	3.8	8	87.9	7.78	.304
.398	7.0	12	86.2	7.72	.445
.499	7.0	10	85.0	7.85	.535
.594	7.0	5	84.0	7.76	.634
.751	2.8	19	82.9	7.61	.750
Styrene (M_1) and *m*-Chlorostyrene (M_2)[c]					
			Cl.[d] %		
0.208	0.4	0.2	2.78		0.0839
.288	.2	1.9	4.16		.1275
.367	2.1	0.1	4.79		.1437
.540	1.6	.4	9.03		.2890
.615	1.1	.6	9.82		.3190
.798	1.5	.5	16.59		.5790
Styrene (M_1) and *p*-Nitrostyrene (M_2)[f]					
			N.[g] %		
0.488	17.5	2	0.20		0.015

[a] The data for the styrene–*p*-methoxystyrene system is omitted since only approximate data could be obtained due to the very large differences in reactivities. This latter system was carried out in pure carbon tetrachloride as a solvent; 0.5% stannic chloride based on monomers; the copolymerization of styrene and *p*-methoxystyrene has been reported by C. Walling, E. R. Briggs, W. Cummings and F. R. Mayo, THIS JOURNAL, **72**, 48 (1950). These authors also reported that *p*-methoxystyrene was much more reactive than styrene. They however used only one monomer charge, presumably 50–50. [b] Corrected for finite conversions. [c] In a 1:1 carbon tetrachloride–nitrobenzene mixture as solvent; 1% stannic chloride. [d] Analyses by Drs. Weiler and Strauss, Oxford, England. [e] Analyses by Mr. H. S. Clark, Urbana, Illinois, and Dr. K. Ritter, Zurich, Switzerland. [f] In pure carbon tetrachloride as a solvent; 2% stannic chloride. [g] Analyses by Dr. R. Schachat, Polytechnic Institute of Brooklyn.

By increasing the rate of dehydration, that is, by removing the *m*-methoxystyrene at a rate of 35 drops per minute instead of 10 drops per minute as suggested by the procedure of reference 6b, the yield increased from 50 to 75%.

Monomers were carefully dried over anhydrous magnesium sulfate or anhydrous calcium sulfate and were distilled under reduced pressure immediately prior to use.

Solvents and Catalyst.—The purification of carbon tetrachloride, nitrobenzene and the stannic chloride catalyst was described in the previous paper.[1]

Experimental Technique.—In general, the copolymerizations were carried out as described in a previous paper.[1] Conversions were calculated from the weight of polymer obtained. A bromine titration useful for determining approximate conversion of styrene was unsatisfactory with most substituted styrenes.

The following formula was used in correcting M_2 for finite conversions

$$M_2 = \frac{M_2'}{2} + \frac{M' - m_2C}{2(1 - C)} \times \text{conversion}$$

where M_2 and M_2' are the corrected and uncorrected values, respectively, for the concentration of M_2 in the monomer mixture, and C is the (molar) conversion.

TABLE II

COPOLYMERIZATION OF STYRENE (M_1) WITH SUBSTITUTED STYRENES (M_2)[a]

M_2	r_1	r_2	$1/r_1$	$\log 1/r_1$	σ
p-OCH_3	(0.01)	(100)	(100)	(2)	−0.268
m-OCH_3	0.90 ± 0.15	1.1 ± 0.15	1.11	0.045	+ .115
p-Cl	2.5 ± .4	0.30 ± .05	0.40	− .39	+ .227
m-Cl	3.3 ± .4	.3 ± .05	.30	− .52	+ .373
m-NO_2[b]	20 ± 4.0	.03 ± .03	.05	−1.30	+ .710

[a] $\rho = -1.7$. [b] *p*-Nitro, see Table I, a 50–50 monomer charge with styrene gave only *ca.* 1.5% of *p*-nitrostyrene in the copolymer.

Results

The data for the copolymerization of styrene with *p*-nitro-, *p*-methoxy-, *m*-nitro-, *m*-methoxy- and *m*-chlorostyrenes are summarized in Tables I and II, Fig. 1. The data for the copolymerization of styrene and *p*-chlorostyrene have previously

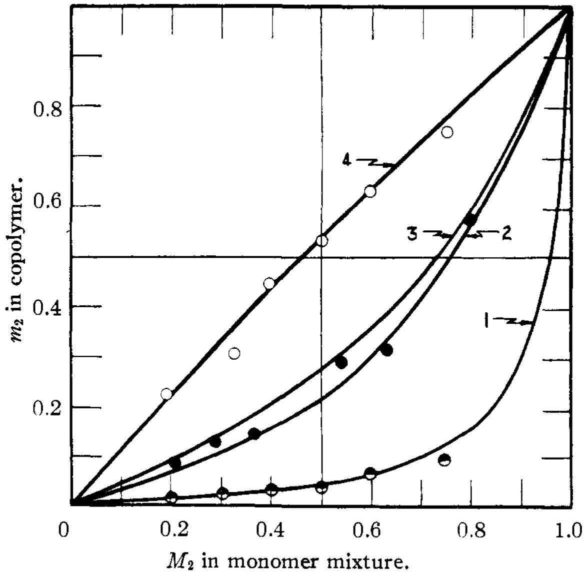

Fig. 1.—Copolymerization of styrene (M_1) with substituted styrene (M_2); 1, ◒, *m*-nitrostyrene; 2, ●, *m*-chlorostyrene; 3, *p*-chlorostyrene; 4 ○, *m*-methoxystyrene, log *r*.

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(11) R. H. Wiley and N. R. Smith, *ibid.*, **70**, 2295 (1948).

(12) H. E. Ungnade and E. F. Orwoll, *Org. Syntheses*, **23**, 11 (1943).

(13) S. Natelson and S. P. Gottfried, THIS JOURNAL, **61**, 1001 (1939).

been reported. A plot of the log $1/r_1$ *vs.* σ is indicated in Fig. 2.

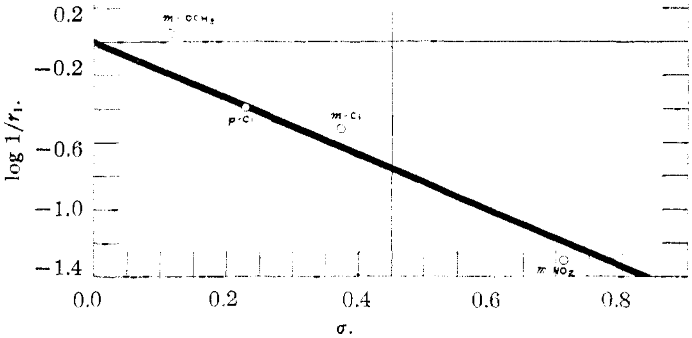

Fig. 2.—Plot of log relative reactivity toward a styrene carbonium ion *vs.* Hammett σ-value for various substituted styrenes.

The data for the copolymerization of *p*-chlorostyrene with *p*-bromo-, *p*-methyl and *m*-methoxystyrenes are summarized in Tables III and IV, Fig. 3. A plot of the log of $1/r_1$ *vs.* σ is indicated in Fig. 4.

TABLE III

COPOLYMERIZATION OF *p*-CHLOROSTYRENE WITH SUBSTITUTED STYRENES

M_2 in monomer mixture[b]	Reaction time (hr.)	Conversion, %	Br,[c] %	Cl,[c] %	m_2
p-Chlorostyrene (M_1) and *p*-Bromostyrene (M_2)[a]					
0.104	0.1	2	4.9	21.6	0.093
.205	.5	10	10.4	19.1	.194
.385	.5	5	20.3	13.5	.400
.594	.5	10	28.8	8.1	.612
p-Chlorostyrene (M_1) and *p*-Methylstyrene (M_2)[d]					
0.177	0.10	6		14.65[e]	0.464
.275	.07	6		10.66	.619
.357	.03	8		8.09	.715
.465	.02	9		7.07	.753
.585	.01	8		3.73	.872
.719	.002	4		1.64	.945
p-Chlorostyrene (M_1) and *m*-Methoxystyrene (M_2)[d]					
0.202	20.0	2.4		15.70[e]	0.394
.308	26.7	2.3		12.78	.508
.402	23.3	3.5		10.95	.577
.503	11.8	2.5		8.45	.680
.602	5.5	2.2		4.27	.837
.750	5.0	3.3		3.04	.883

[a] In a 2:1 carbon tetrachloride–nitrobenzene mixture as a solvent; 2% stannic chloride. [b] Corrected for finite conversions. [c] Analyses by Dr. K. Ritter, Zurich, Switzerland. [d] In a 1:1 carbon tetrachloride–nitrobenzene mixture as solvent; 1% stannic chloride. [e] Analyses by Drs. Weiler and Strauss, Oxford, England.

TABLE IV

COPOLYMERIZATION OF *p*-CHLOROSTYRENE (M_1) WITH SUBSTITUTED STYRENES (M_2)[a]

M_2	r_1	r_2	$1/r_1$	log $1/r_1$	σ
p-CH$_3$	0.22 ± 0.05	4.5 ± 0.7	4.55	0.658	−0.170
m-OCH$_3$	0.38 ± .05	2.6 ± .4	2.63	.420	+ .115
p-Br	1.0 ± .1	1.0 ± .1	1.0	0	+ .232
p-H	0.35 ± .05	2.2 ± .5	2.8	.447	0

[a] $\rho = -1.7$.

The data for the copolymerization of α-methylstyrene with *p*-dimethylamino-, *p*-methoxy- and *m*-methoxystyrenes are summarized in Tables V and VI, Fig. 5. Calculated values of *p*-methyl- and styrene are included. The following method was used for the calculated values. The reactivities of styrene, *p*-methylstyrene and α-methylstyrene with *p*-chlorostyrene are $r_1 = 2.5$ in Table II; $r_2 = 4.5$ in Table IV; and $r_1 = 15.5$ (ref. 1). Thus r_1 for the system α-methylstyrene (M_1), styrene (M_2) is estimated to be 15.5/2.5 or 6.2 (log 1/6.2 = −0.79); r_1 for the system α-methylstyrene (M_1), *p*-methylstyrene (M_2) is 15.5/4.5 or 3.4 (log 1/3.4 = −0.53).

The reactivity ratios and their probable errors were obtained by the use of a previously described procedure.[14] In this method, the experimental points are fitted with two curves which represent the limits of reasonable values of r_1 and r_2. The reactivity ratios are calculated for the curves and the averages of these limiting values are taken to be the most probable

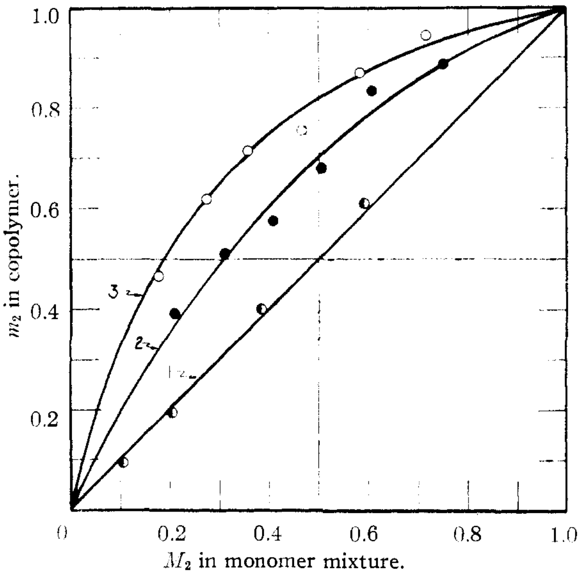

Fig. 3.—Copolymerization of *p*-chlorostyrene (M_1) with substituted styrenes (M_2): 1, ◐, *p*-bromostyrene; 2, ●, *m*-methoxystyrene; 3, ○, *p*-methylstyrene.

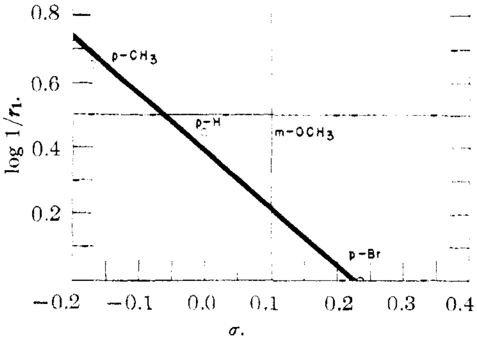

Fig. 4.—Plot of log relative reactivity toward a *p*-chlorostyrene carbonium ion *vs.* Hammett σ-value for various substituted styrenes.

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[14] T. Alfrey, A Goldberg and W. P. Hohenstein, This Journal, **68**, 2464 (1946).

values of r_1 and r_2. The variations of the latter from the limiting values are accepted as the probable errors.

TABLE V

COPOLYMERIZATION OF α-METHYLSTYRENE (M_1) WITH SUBSTITUTED STYRENES (M_2)

M_2 in monomer mixture[b]	Reaction time (hr.)	Conversion, %	N.[c] %		m_2
α-Methylstyrene (M_1) and *p*-Dimethylaminostyrene (M_2)[a]					
0.267	2	0.7	8.18		0.831
.479	2	2.3	9.10		.946
.532	2	2.7	8.85		.915
.050	2 days	1	6.88		.677
.134	2 days	3	9.22		.962
.658	1 day	2	9.26		.967
α-Methylstyrene (M_1) and *p*-Methoxystyrene (M_2)[d]					
			C. %[f]	H. %	
0.055	0.2	13.4[d]	87.98	8.38	0.212
.166	.2	22.2[d]	84.80	8.08	.563
.307	5 days	1.0[e]	81.67	8.04	.847
.428	20	2.2[e]	80.92	7.64	.847
.567	5 days	2.9[e]	80.76	7.54	.978
.681	19.5	4.1[e]	80.65	7.77	.966
α-Methylstyrene (M_1) and *m*-Methoxystyrene (M_2)[g]					
0.200	0.02	15	90.8[h]	8.62	0.051
.305	.02	11	90.1	8.36	.113
.403	Secs.	6	90.0	8.26	.121
.502	Secs.	5	89.6	8.44	.125
.615	Secs.	3	88.0	8.26	.293
.750	0.1	3	87.3	8.08	.370

[a] In pure carbon tetrachloride as solvent; 2% stannic chloride. [b] Corrected for finite conversions. [c] Analyses by Dr. R. Schachat, Polytechnic Institute of Brooklyn. [d] In pure carbon tetrachloride as solvent; 1% stannic chloride. [e] In pure carbon tetrachloride; 0.2% stannic chloride. [f] Analyses by Mr. H. S. Clark, Urbana, Illinois. [g] In a 1:1 carbon tetrachloride–nitrobenzene mixture as a solvent; 1% stannic chloride. [h] Analyses by Drs. Weiler and Strauss, Oxford, England.

TABLE VI

COPOLYMERIZATION OF α-METHYLSTYRENE (M_1) WITH SUBSTITUTED STYRENES (M_2)[a]

M_2	r_1	r_2	$1/r_1$	log $1/r_1$	σ
p-OCH_3	0.30 ± 0.1	15 ± 5	3.3	0.518	−0.268
p($(CH_3)_2N$)	0.035 ± 0.015	31 ± 19	28.6	1.454	− .205
m-OCH_3	5 ± 1	0.3 ± 0.1	0.20	−0.70	+ .115
p-Cl	15 ± 1.5	0.35 ± 0.05	0.067	1.174	+ .227

[a] $\rho = -1.7$; *p*-CH_3 ($r_1 = 3.3$) and *p*-H ($r_1 = 6.0$) are also plotted in Fig. 6. These values are calculated; see section on results.

Due to the low reactivity of *m*-nitrostyrene, it was not possible to obtain a precise value for r_2 and hence r_1. Pure *m*-nitrostyrene did not polymerize under the conditions employed and mixtures rich in *m*-nitrostyrene polymerize very slowly.

Discussion of Results

In a previous paper reference was made to two previously considered mechanisms for ionic polymerization. According to Fontana and Kidder,[15] the over-all rate depends on the total concentration of active center (equal to the co-catalyst concentration), the fraction of active centers that are complexed with monomer (an equilibrium value) and the rate constant for rearrangement of the monomer-active center complex. In the scheme of Mayo and Walling,[16] adapted to this system, the first rate-determining step is the ionization of the active center (ion pair) and the second rate determinant is the ratio, rate of propagation/rate of propagation + rate of recombination.

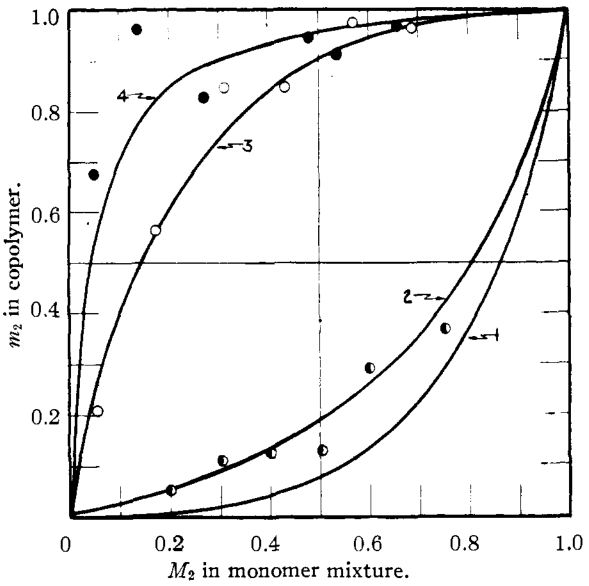

Fig. 5.—Copolymerization of α-methylstyrenes (M_1) with substituted styrenes (M_2): 1, *p*-chlorostyrene; 2, ◐, *m*-methoxystyrene; 3, ○, *p*-methoxystyrene; 4, ●, *p*-dimethylaminostyrene.

A second mechanism assumes a steady state concentration of carbonium ions.[17] This latter mechanism may be more probable in our system with a weak catalyst such as stannic chloride and a solvent mixture of carbon tetrachloride and nitrobenzene in which the dielectric constant is fairly high.

One attempt to treat the radical catalyzed copolymerization of monomers quantitatively was that of Walling, Briggs, Wolfstirn and Mayo.[18] These authors studied the effect of nuclear substituents on the reactivity of styrene. They found that when the substituted styrene monomers were copolymerized with styrene a linear correspondence was obtained between the σ-values of Hammett[5] and the relative reactivity ratios. Copolymerizations of these substituted styrenes with methyl methacrylate and maleic anhydride did not give similar results. On the contrary, for negative values of sigma, *p*-methoxy, *p*-dimethylamino and *p*-methyl substituents, there was no consistent relation between sigma and the relative reactivity. Especially large reactivities were found for *p*-methoxy- and *p*-dimethylamino-α-methylstyrenes when these were copolymerized with maleic anhydride. This apparent anomaly was explained by a suggestion that the major driving force for strong alternation arises from contributions to the transition

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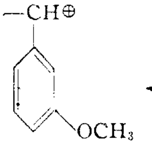
[15] C. M. Fontana and G. A. Kidder, THIS JOURNAL, **70**, 3745 (1948).

[16] F. R. Mayo and C. Walling, *ibid.*, **71**, 3845 (1949).

[17] (a) P. H. Plesch, *J. Chem. Soc.*, 543 (1950); (b) D. D. Eley and A. W. Richards, *Trans. Faraday Soc.*, **45**, 425 (1949).

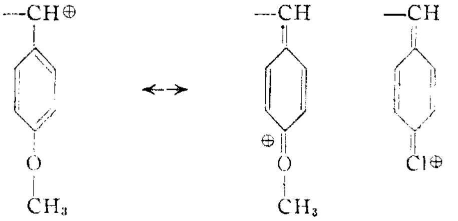
[18] C. Walling, E. R. Briggs, K. B. Wolfstirn and F. R. Mayo, THIS JOURNAL, **70**, 1537 (1948).

state of forms in which actual electron transfer between radical and monomer (or *vice versa*) has taken place. Thus, for the methoxy, dimethylamino and methyl substituted monomers, a large number of resonance forms arise in the transition state.



In Fig. 1, it can be seen that the plot for *p*-chloro-, *m*-chloro- and *m*-nitrostyrenes is a reasonable straight line. No appreciable copolymerization occurs with *p*-nitrostyrene, and *p*-methoxystyrene is far more reactive than would be predicted. These latter two values are not recorded on the figure. One of the difficulties of getting sufficient copolymer composition data for cationic catalysis is well illustrated here: namely, the very large differences in reactivity of monomers. This wide spread in reactivities makes it impossible to compare the reactivities of more than a small number of monomers. It is clear why *p*-nitrostyrene is very unreactive because of the strong electron-withdrawing properties of the nitro group and there is good reason to suspect why *p*-methoxystyrene is more reactive than predicted.

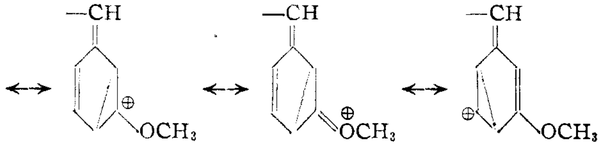
Mayo and Walling, using the data of Norris and Banta,[19] of Hughes, Ingold and Taher,[20] and of Branch and Nixon[21] have pointed out that where the reaction intermediate involves a carbonium ion, special resonance forms are available due to the presence of a mobile electron pair in substituents such as the methoxyl group. In the studies just mentioned, the rates for the solvolysis of *p*-methoxy, *p*-alkyl and *p*-phenylbenzhydryl and triphenylmethyl chlorides were greater than would be predicted by the use of Hammett's σ-values. It is apparent that a similar situation may exist in carbonium ion copolymerization. A larger number of nearly equivalent resonance forms can be written for the carbonium ions of the *p*-methoxy- and *p*-dimethylaminostyrene monomers than for that of *p*-chlorostyrene.



A B C

The contribution of C to the stabilization of the *p*-chlorobenzyl carbonium ion is probably much less than that of B for the *p*-methoxybenzyl carbonium ion. *m*-Methoxystyrene has a slightly greater reactivity than would have been predicted on the basis of the σ-value for the *m*-methoxy substituent.

In Fig. 4, log $1/r_1$ for the monomers (M_2) *p*-bromo, *m*-methoxy, *p*-methylstyrene and styrene copolymerized with *p*-chlorostyrene (M_1) are plotted against sigma. Again the *m*-methoxystyrene shows the greatest deviation from a straight line. *This anomaly with m-methoxystyrene may well arise from a consideration of such structures as IV and V, heretofore considered as very high-energy forms.*



IV V VI

Since a structure such as IV may very well be stabilized by the methoxy group as indicated, significant contributions to the energy of the carbonium ion may be due to such hybrids. Structures such as VI would not be expected to contribute to any extent. It has recently been demonstrated[22] by other workers that the effect of a methoxy group on a meta position is greater than one would ordinarily predict as determined by nuclear bromination.

In Table V are summarized the data obtained from copolymerization of α-methylstyrene with *p*-chloro-, *m*-methoxy-, *p*-methoxy- and *p*-dimethylaminostyrenes. Although differences in reactivity are qualitatively in the same order as the σ-values (except for *p*-dimethylaminostyrene) a plot of log $1/r_1$ *vs.* σ for these experiments does not give a good straight line. However, using estimated values of r_1 for α-methylstyrene (M_1) with styrene and *p*-methylstyrene, and the experimental value for *p*-chloro, a straight line is obtained.

Assuming that the propagation step in carbonium ion polymerization involves the reaction of an ion pair with a monomer, it would appear that the monomer reactivities approximate Hammett's σ-series except for the methoxy and p-dimethylamino substituted monomers. This is an indication that there is sufficient separation of charge in the ion-pair in this system to prevent the anion from changing the relative order of carbonium ion reactivities that would be predicted on the basis of other reactions. Since there is involved the acid strength of the carbonium ion and the base strengths of the catalyst anion and the monomer, it is *a priori* difficult to determine what the driving force is in this reaction. The copolymerization experiments reported here and elsewhere emphasize, however, the powerful effects of monomer base strengths as well as the resonance of the carbonium ion adduct in the transition state. The concept of a concerted reaction seems applicable here.

It is of interest to compare this data with that recently reported by Swain and Langsdorf.[23] They have proposed that in displacement reactions, ρ in the Hammett scheme is not a constant but continues to change with different σ-values. In the reaction of benzyl chlorides with trimethylamine in benzene solution, a plot of log k/k_0 *vs.* σ for substituent groups in the para positions of the benzyl chloride is drawn as a curve and not as a straight line. Meta substituents are plotted to give a separate

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[19] J. F. Norris and C. Banta, THIS JOURNAL, **50**, 1804 (1928).

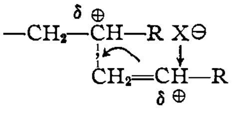
[20] E. D. Hughes, C. K. Ingold and N. A. Taher, *J. Chem. Soc.*, 949 (1940).

[21] G. E. K. Branch and A. C. Nixon, THIS JOURNAL, **58**, 2499 (1936).

[22] P. B. D. deLaMare and C. A. Vernone, *J. Chem. Soc.*, 1764 (1951).

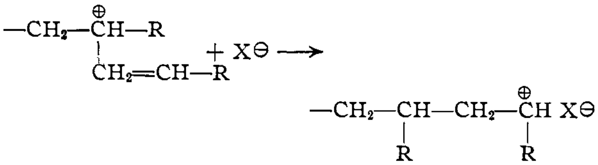
[23] C. G. Swain and W. P. Langsdorf, Jr., THIS JOURNAL, **73**, 2813 (1951).

curve. It is of interest to note that Fig. 6 could likewise be drawn as a curve and if σ values for the *p*-methoxy and *p*-dimethylamino group were included in Fig. 2, a similar curve to that obtained by Swain would be obtained. One might interpret these results to indicate that the addition of R^+X^- to an olefin is also termolecular with a transition state somewhat similar to that proposed for concerted displacement reactions as indicated. With substituent groups in our system, bond breaking (polarization of double bonds by positive portion of ion pair) is largely taking place as indicated by the negative ρ's.



$$\begin{matrix} -CH_2-\overset{\delta\oplus}{C}H-R\ X^{\ominus} \\ CH_2=\underset{\delta\oplus}{C}H-R \end{matrix}$$

Groups such as *p*-methoxy and *p*-dimethylamino which will stabilize the partial positive charge on carbon in the transition state would change the ρ to even a larger negative value. This evidence points to an ion pair in the propagation step in which the anionic fragment is utilized in the bond polarization. A π-complex scheme may also be applicable. The σ-plots seem applicable in this case as carbon X in the transition state would bear a partial positive charge.



$$\begin{matrix} -CH_2-\overset{\oplus}{C}H-R \\ CH_2=CH-R \end{matrix} + X^{\ominus} \longrightarrow -CH_2-\underset{R}{CH}-CH_2-\underset{R}{\overset{\oplus}{C}H}\ X^{\ominus}$$

Since α-methylstyrene is more reactive with *p*-chlorostyrene than is *p*-methylstyrene, it appears that the methyl group in the α-position has a greater activating effect than has the *p*-methyl group.

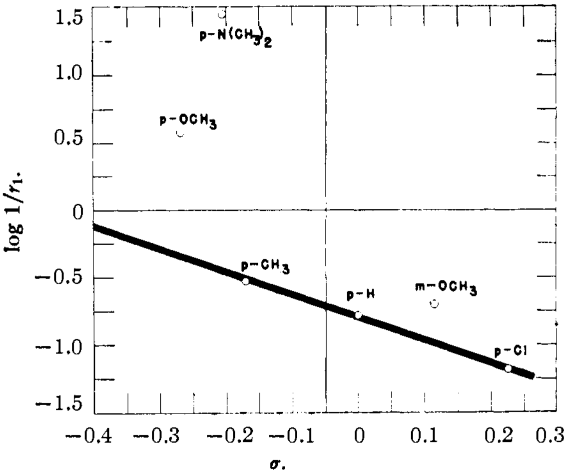


Fig. 6.—Plot of log relative reactivity towards an α-methylstyrene carbonium ion *vs.* Hammett σ-value for various substituted styrenes.

In contrast with radical copolymerizations no alternation tendency has been found for systems subject to acid catalysis. Due to the low activation energy of reactive monomers in acid-catalyzed systems, disubstituted monomers having electron rich double bonds can compete favorably with monosubstituted monomers for growing carbonium ions. Disubstitution does appear to reduce the reactivity. Thus, *p*-methoxystyrene is more reactive with styrene than is anethole with *o*-chlorostyrene.[24]

[24] T. Alfrey, Jr., L. Arond and C. G. Overberger, *J. Polymer Sci.*, **4**, 539 (1949).

BROOKLYN, N. Y.

[CONTRIBUTION FROM THE NEW PRODUCTS DEVELOPMENT LABORATORY, GENERAL ELECTRIC COMPANY, CHEMICAL DIVISION]

Acetylenic Silicon Derivatives*

BY KURT C. FRISCH AND ROBERT B. YOUNG

RECEIVED MARCH 27, 1952

Acetylenic silicohydrocarbons and chlorosilanes were prepared by treating acetylenic Grignard compounds with chlorosilanes in the presence of cuprous chloride as a catalyst. The acetylenic chlorosilanes were converted first to the acetoxysilanes or were directly hydrolyzed to the corresponding silanols or siloxanediols without rupture of the $\equiv C-Si$ bond. Some addition products of the acetylenic derivatives were prepared.

Very little is known concerning the chemistry of acetylenic silicon derivatives. Volnov and Reutt[1] prepared (phenylethynyl)-triethoxysilane and bis-(phenylethynyl)-diethoxysilane by the reaction of phenylethynylmagnesium bromide with ethyl orthosilicate

$$C_6H_5C\equiv CMgBr + Si(OC_2H_5)_4 \longrightarrow C_6H_5C\equiv C-Si(OC_2H_5)_3 + (C_6H_5C\equiv C)_2Si(OC_2H_5)_2$$

These authors concluded that the phenylethynyl group was only weakly bound to silicon since it decomposes on hydrolysis with formation of silica, ethanol and phenylacetylene.

Hexaethynyldisiloxane $[(HC\equiv C)_3Si]_2O$ was also prepared by the same investigators by treating ethynylmagnesium bromide with silicon tetrachloride and hydrolyzing the reaction product. Hexaethynyldisiloxane also decomposes in cold water, yielding acetylene and silica, confirming apparently the labile behavior of the carbon-silicon bond in which one of the carbon atoms of the triple bond is linked to silicon.

Boldebuck[2] in a recent patent described the preparation of "esters of ethynyl siliconic acid." Ethoxytriethynylsilane, diethoxydiethynylsilane and triethoxyethynylsilane were described. These compounds were prepared by reaction of sodium

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* Presented at the Atlantic City Meeting of the A. C. S., September, 1952.

[1] Y. N. Volnov and A. Reutt, *J. Gen. Chem.* (*U.S.S.R.*), **10**, 1600 (1940).

[2] E. N. Boldebuck, U. S. Patent 2,551,924 (to Pittsburgh Plate Glass Co.) (1951).