TABLE I

RELATIVE REACTIVITIES AND MONOMER REACTIVITY RATIO PRODUCTS (r_1r_2)

Monomer	Relative reactivities toward Styrene radical	Methacrylate radical	(r_1r_2) With styrene	With methacrylate
Styrene	1.00	1.00	1.00	0.24 ± 0.01
α-Vinylpyridine	1.82 ± 0.08	1.17 ± 0.08	0.625 ± 0.052	.340 ± .035
α-Vinylthiophene	2.86 ± .20	....	1.09 ± .18	....
o-Chlorostyrene	1.78 ± .06	.97 ± .06	.919 ± .063	.685 ± .065
α-Methylstyrene	....	.97 ± .06	....	.070 ± .007

and also the monomer reactivity ratio products (r_1r_2's) which serve as qualitative measures of the tendencies of the two monomers to alternate in copolymerization.

It may be seen from Table I that the monomers are all more reactive toward the styrene-type radical, than styrene and lie in the order styrene < *o*-chlorostyrene < α-vinylpyridine < α-vinylthiophene. Further, only α-vinylpyridine shows an appreciable tendency to alternate with a r_1r_2 value significantly smaller than unity. It is of interest that, of the three chlorostyrenes, the *o*-chloro is the most reactive, reactivities[2] lying in the order *p*-Cl (1.35) < *m*-Cl (1.56) < *o*-Cl (1.78). In reactivity toward the methacrylate radical, the three styrenes are indistinguishable and α-vinylpyridine is slightly more reactive. Apparently, the greater reactivity of α-vinylpyridine and *o*-chlorostyrene (as shown in copolymerization with styrene) is counteracted by a lesser tendency to alternate in copolymerization with methacrylate (larger r_1r_2 values) than is shown by styrene. The very small r_1r_2 value for α-methylstyrene is probably due to its reluctance to polymerize alone (a 1:4 methacrylate-α-methylstyrene mixture yields only 7–10% polymer in six hundred hours) rather than to an unusually high reactivity toward the methyl methacrylate type radical.

Experimental

Styrene, methyl methacrylate, α-methylstyrene and α-vinylpyridine were commercial materials, distilled *in vacuo* and stored in the ice-box before use. The preparation and properties of the samples of *o*-chlorostyrene[7] and α-vinylthiophene[8] are described elsewhere.

Polymerizations were carried out at 60° in sealed tubes in absence of air, using, usually, 0.08 mole total monomers and 0.5 mole % benzoyl peroxide. All polymers were benzene soluble, and were worked up by the frozen benzene technique[9] using petroleum ether as a precipitant.

Summary

1. Monomer reactivity ratios have been determined for the copolymerization at 60° of styrene with α-vinylpyridine, α-vinylthiophene, and *o*-chlorostyrene and of methyl methacrylate with α-vinylpyridine, *o*-chlorostyrene and α-methylstyrene, and the results are discussed.

(7) Walling and Wolfstirn, *ibid.*, **69**, 852 (1947).

(8) Strassburg, Gregg, and Walling, *ibid.*, **69**, 2141 (1947).

(9) Lewis and Mayo, *Ind. Eng. Chem., Anal. Ed.*, **17**, 134 (1945).

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Copolymerization. XII. The Effect of *m*- and *p*-Substitution on the Reactivity of α-Methylstyrene toward the Maleic Anhydride Type Radical

BY CHEVES WALLING, DEXTER SEYMOUR AND KATHERINE B. WOLFSTIRN[1]

A study[1a] of the copolymerization of methyl methacrylate with a series of *m*- and *p*-substituted styrenes has shown that, for most of the styrenes studied, relative reactivities toward the methyl methacrylate type radical followed quite well the order found by Hammett[2] for ionic-type side-chain reactions with a small positive rho value, *i. e.*, increasing reactivity with the introduction of increasingly electron withdrawing groups. However, anomalously high reactivities were observed (in increasing order) for *p*-methyl-, *p*-methoxy- and *p*-dimethylaminostyrenes.

These enhanced reactivities were shown to parallel the increased tendencies of these styrenes to form colored complexes with molecules such as maleic anhydride and chloranil, and it was suggested that they were due to the availability of additional resonance forms in the transition state of the copolymerization reaction in which an electron had been transferred from the styrene to the attacking carbonyl-conjugated radical. Existence of similar forms in the complexes in which an electron has been transferred to the conjugated carbonyl system has already been proposed by Weiss.[3]

Since these observations throw valuable light on the nature of the "alternating tendency" in

(1) Present address, Bell Telephone Laboratories, Summit, N. J.

(1a) Walling, Briggs, Wolfstirn and Mayo, THIS JOURNAL, **70**, 1537 (1948).

(2) Hammett, "Physical Organic Chemistry," McGraw–Hill Book Co., Inc., New York, N. Y., 1940, Chap. VII.

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

copolymerization[4,5,6] it seemed desirable to carry out further studies with a monomer showing a greater tendency to alternate with styrene, in which such resonance forms might be even more important. This paper reports such a study, using substituted α-methylstyrenes and maleic anhydride, probably the extreme type of such a monomer.[6,7,8]

Due to the high tendency of styrenes and maleic anhydride to alternate in copolymerization, both monomer reactivity ratios are essentially zero. Accordingly, it is not possible to investigate relative reactivities by simple copolymerization experiments, and recourse must be had to competitive reactions in three-component systems composed of two styrenes and maleic anhydride. In such a system, since four of the six monomer reactivity ratios are very small, the polymer consists of chains in which maleic anhydride residues alternate regularly with one or the other styrene and the complex terpolymerization equation[9] can be greatly simplified.[10] Under such conditions virtually the only[11] reaction which consumes either styrene is attack by the maleic anhydride type radical. Designating the two styrenes as M_1 and M_2 and the rate constants for their respective reactions with maleic anhydride as k_1 and k_2, this condition leads to the simple differential equation

$$\frac{d[M_1]}{d[M_2]} = \frac{k_1[M_1]}{k_2[M_2]} \qquad (1)$$

which on integration yields

$$\log [M_1]_0/[M_1] = k_1/k_2 \log [M_2]_0/[M_2] \qquad (2)$$

with zero subscripts indicating initial concentrations. Carrying out such a polymerization to partial conversion, determining $[M_1]$ and $[M_2]$ by analysis of either the polymer, or, as proves more convenient in these systems, the unreacted styrenes, and substituting these values into (2) permits a calculation of k_1/k_2, the desired ratio of reactivities of the two styrenes toward the maleic anhydride type radical. By comparing a series of substituted α-methylstyrenes with one selected as a standard, the relative reactivities of the whole series toward the maleic anhydride type radical may thus be determined.

Experimental

Materials

Maleic anhydride was Eastman Kodak Co. material, m. p. 54.0–57.0°, used without further purification.

α-Methylstyrene was purified by fractionating commercial material through a 14-cm. column packed with glass helices. The fraction used had the following constants: b. p. 69.0–69.2° at 27 mm., $n^{20}D$ 1.5383. The material was always used shortly after distillation since it tended to oxidize to acetophenone and formaldehyde even when stored in a stoppered bottle in the refrigerator.

α-*p*-Dimethylstyrene was purified by fractionating commercial material through a 45-cm. helices-packed column. The fraction used had b. p. 72–3° at 11.5 mm. $n^{20}D$ 1.5334.

Substituted α-Methylstyrenes.—The syntheses and properties of the other α-methylstyrenes are described elsewhere.[12]

Polymerizations and Analyses

Polymerizations were carried out by heating mixtures of two α-methylstyrenes and maleic anhydride in sealed tubes at 60° in the presence of benzoyl peroxide and absence of air.[4] In general 0.1 mole of mixed styrenes (in 1:2, 1:1, or 2:1 molar ratios), 0.05 to 0.1 mole maleic anhydride, and 0.16–0.18 millimole of benzoyl peroxide were used in each experiment, and heating times were adjusted to consume 50–90% of the maleic anhydride. As might be expected, the products under these conditions yielded viscous solutions and had the properties of high polymers rather than Diels–Alder adducts.[13]

Although reactivities were ultimately related to α-methylstyrene, most reactions were actually run on mixtures of α-methylstyrenes with α,*p*-dimethylstyrene, since this compound proved to be more stable to storage than our sample of α-methylstyrene. Due to its high reactivity, it was found necessary to compare *p*-dimethylamino-α-methylstyrene with *p*-methoxy-α-methylstyrene and also to dilute the reaction mixture with 15 cc. of acetic anhydride to moderate the reaction.

Analyses were carried out by determining the amount and composition of the unreacted styrenes. After removal from the 60° bath, tubes were frozen in liquid nitrogen, wrapped in cellophane, crushed, and dropped into a one l. flask containing 200 cc. of 1 *N* sodium hydroxide solution and 0.5 g. hydroquinone. After shaking for an hour at room temperature, during which time the polymer usually dissolved, the residual styrenes were steam distilled into a graduated water separator (Dean and Stark trap) modified so that liquids either lighter or heavier than water could be separated. When distillation was complete, the volume of styrenes was noted and they were separated from the water layer, dried over anhydrous potassium carbonate, and analyzed. In the case of the systems containing *p*-cyano-α-methylstyrene, sodium bicarbonate was substituted for sodium hydroxide to minimize hydrolysis of the nitrile. For the system *p*-dimethylamino-α-methylstyrene-*p*-methoxy-α-methylstyrene, the unreacted monomers were steam-distilled into a 500-cc. flask which was next attached to a liquid-liquid extractor and the styrenes extracted for twenty-four hours with ether containing a little *t*-butylcatechol. Following removal of the ether (first at atmospheric pressure and then by freezing the mixture at −5° and pumping for five hours at 2 mm.) the styrenes were analyzed for nitrogen.

Compositions of the unreacted styrene mixtures containing chlorine, bromine or nitrogen were determined by

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(4) Mayo and Lewis, THIS JOURNAL, **66**, 1594 (1944).

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

(6) Mayo, Lewis and Walling, THIS JOURNAL, **70**, 1529 (1948).

(7) Wagner-Jauregg, *Ber.*, **63**, 2313 (1930).

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

(9) (a) Alfrey and Goldfinger, *J. Chem. Phys.*, **12**, 322 (1944); (b) Walling and Briggs, THIS JOURNAL, **67**, 1774 (1945).

(10) The simplification arising when one or two monomer reactivity ratios are zero has been already discussed by Alfrey and Goldfinger, *J. Chem. Phys.*, **14**, 115 (1946).

(11) When this project was undertaken preliminary measurements on the system styrene–maleic anhydride had indicated a monomer reactivity ratio for the styrene radical of 0.15, too small for the comparison of ordinary copolymerizations, but enough to introduce errors into the kinetics described above. Accordingly, a series of α-methylstyrenes were employed since the α-methylstyrene radical shows very little tendency to add to its own monomer (*cf.* Walling, Briggs and Wolfstirn, THIS JOURNAL, **70**, 1543 (1948). Subsequent work[6] has shown that the monomer reactivity ratio is actually less than 0.01, making the precaution unnecessary.

(12) Seymour and Wolfstirn, THIS JOURNAL, **70**, 1177 (1948).

(13) Tomayo-Viguera, *Anales fis. chim.*, **38**, 184 (1942). By heating maleic anhydride and α,*p*-dimethylstyrene in the presence of 1% trinitrobenzene as a polymerization inhibitor, we were able to isolate, besides considerable dioxane-soluble polymer, a small amount of a high-melting (>230°) material relatively insoluble in dioxane and giving solutions of low viscosity ([η] = 0.07). This may represent the Diels–Alder type product.

elementary analysis. Mixtures of α,*p*-dimethylstyrene with *p*-fluoro- or *p*-methoxy-α-methylstyrene were analyzed by index of refraction, the linear relation between index and volume fraction having been established from known mixtures.

α-Methylstyrene and α,*p*-dimethylstyrene differ too little in index of refraction for accurate analysis and so mixture compositions were determined by melting point using a melting-point curve constructed from the data of Table I.

TABLE I

MELTING POINTS OF KNOWN α-METHYLSTYRENE–α,*p*-DIMETHYLSTYRENE MIXTURES

Vol. % dimethylstyrene	M. p., °C.	Vol. % dimethylstyrene	M. p., °C.
0.0	−24.5	55.6	−52.0
16.6	−31.8	62.5	−47.7
28.6	−36.8	71.4	−43.0
37.5	−42.4	83.2	−36.6
44.5	−49.5	100.0	−28.0
50.0	−52.8		

All melting points were taken as the "flats" observed in the warming curve of styrene mixtures measured with a Leeds and Northrup potentiometer using a copper-constantan thermocouple with a melting ice reference junction. This combination gives readings to ±0.2°.

Calculation of Experimental Errors.—The accuracies of the analytical methods were tested for the systems α-methylstyrene–*p*-chloro-α-methylstyrene and α-methylstyrene–α,*p*-dimethylstyrene by putting up tubes similar to those used in the polymerizations, but working them up without heating. Results are listed in Table II.

TABLE II

BLANK EXPERIMENTS ON α-METHYLSTYRENE MIXTURES

Total monomer volume, cc. Calcd.	Total monomer volume, cc. Found	Vol. % α-Methylstyrene Calcd.	Vol. % α-Methylstyrene Found
With α,*p*-Dimethylstyrene			
13.6	13.4	46.8	45.0
13.6	13.4	47.2	52.5
13.8	13.8	46.8	44.5
With *p*-Chloro-α-methylstyrene			
11.9	11.7	47.6	47.2
11.6	11.5	48.0	49.0
12.0	11.9	48.9	49.4

Results of actual terpolymerization experiments are listed in Table III. Relative reactivities were calculated from each experiment by Equation (2) and averaged for each pair. Experimental error was taken as the standard deviation of the separate experiments for each pair from this mean. Results, all referred to α-methylstyrene as standard,[14] are listed in Table IV. The given experimental errors, in general, correspond to 1–5% errors in monomer isolation and analysis, in reasonable agreement with the blank runs of Table II. In the case of the *p*-cyano-α-methylstyrene system, however, errors were definitely larger. Whether the difficulty was due to the analytical method or other causes was not determined before the sample of *p*-cyano-α-methylstyrene was exhausted.[15] The high reactivity of *p*-dimethylamino-α-methylstyrene, and the rather complex isolation technique which was necessary permit only the assignment of a minimum value for its relative reactivity.

TABLE III

REACTION OF MIXED α-METHYLSTYRENES (M_1 AND M_2) WITH MALEIC ANHYDRIDE (M_3) AT 60°

$[M_1]_0$[a]	$[M_2]_0$[a]	$[M_3]_0$[a]	Time, hr.	$[M_1]$[a]	$[M_2]$[a]
α-Methylstyrene (M_1)–α,*p*-dimethylstyrene (M_2)					
49.4	49.5	49.9	20	31.8	24.3
49.1	49.5	49.9	35	30.9	20.3
32.1	64.8	100.4	7.5	23.0	12.3
64.6	32.4	100.0	7.5	20.1	4.63
α-Methylstyrene (M_1)–*p*-chloro-α-methylstyrene (M_2)					
49.6	49.7	50.0	22	31.0	34.8
65.4	32.4	100.3	20	17.17	11.05
32.5	65.4	99.9	16	13.06	31.6
α,*p*-Dimethylstyrene (M_1)–*p*-fluoro-α-methylstyrene[b] (M_2)					
49.8	49.9	49.9	16.3	31.1	35.1
65.8	32.7	100.0	4.75	10.77	13.68
31.7	65.9	99.9	6.83	4.12	30.8
α,*p*-Dimethylstyrene (M_1)–*p*-bromo-α-methylstyrene (M_2)					
50.0	50.0	50.1	2.33	24.9	38.2
66.0	33.0	100.0	5.75	10.37	17.20
32.8	65.2	99.9	3.66	6.19	29.7
32.9	65.8	100.0	1.50	11.08	37.2
α,*p*-Dimethylstyrene (M_1)–*m*-bromo-α-methylstyrene (M_2)					
49.7	51.5	50.0	23.25	16.68	26.0
66.9	33.6	100.0	5.25	12.24	12.82
33.1	65.9	100.0	9.20	4.55	24.8
α,*p*-Dimethylstyrene (M_1)–*p*-cyano-α-methylstyrene (M_2)					
50.3	45.1	49.9	11.0	27.2	25.5
67.0	28.0	99.9	6.25	21.9	12.23
57.6	32.0	99.9	8.5	23.4	16.50
33.4	65.0	100.0	24.25	1.85	27.4
α,*p*-Dimethylstyrene (M_1)–*p*-methoxy-α-methylstyrene (M_2)					
48.4	49.3	50.0	[c]	45.7	29.0
48.5	49.0	50.0	1.5	42.6	13.43
31.6	64.6	99.4	1.17	23.6	0.98
p-Methoxy-α-methylstyrene (M_1)–*p*-dimethylamino-α-methylstyrene (M_2)					
66.5	58.9	100.0	0.33	62.7	16.10
32.3	26.6	99.9	0.17	32.3	7.71

[a] In millimoles. [b] Monomer contained 2 wt. % *p*-fluorobromobenzene, and results have been corrected accordingly. [c] Experiment was intended as blank, but polymerization occurred on standing at room temperature.

Discussion

In Table IV are listed relative reactivities of the eight α-methylstyrenes toward the maleic anhydride type radical compared with the relative reactivities of the corresponding styrenes toward the methyl methacrylate and styrene type radicals reported previously.

The striking feature of Table IV is the high reactivity of the first three styrenes, which paral-

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[14] In the case that the original comparison was not with α-methylstyrene, the experimental errors in both of the ratios involved were taken into account, using the usual formulas for the propagation of error.

[15] If the difficulty is analytical, it most probably results from failure to recover all of the unreacted *p*-cyano-α-methylstyrene. In this case the apparent reactivity of this monomer is too high and the true value may be near the lower limit indicated in Table IV.

TABLE IV

RELATIVE REACTIVITIES OF STYRENES AND α-METHYLSTYRENES TOWARD VARIOUS RADICALS IN COPOLYMERIZATION

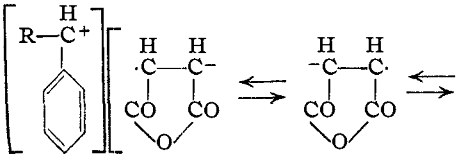
	Attacking radical		
Substituent[a]	Maleic anhydride	Methyl methacrylate	Styrene
p-$N(CH_3)_2$	>300	2.44	0.98
p-OCH_3	18.5 ± 4	1.72	0.86
p-CH_3	1.72 ± 0.12	1.23	..
None	1.00	1.00	1.00
p-F	0.72 ± .10	..	..
p-Cl	.79 ± .02	1.20	1.35
p-Br	.73 ± .15	1.27	1.44
m-Br	.96 ± .14	1.04	1.82
p-CN	.96 ± .57	2.27	3.57

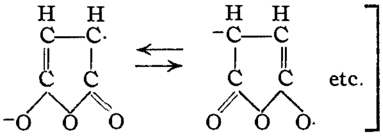
[a] On α-methylstyrene in second column, on styrene in third and fourth.

lels, but is much larger than, that noted previously in connection with reactivity toward the methacrylate radical.[1a] Thus, this increased reactivity, which parallels the tendencies of these styrenes to form colored molecular complexes with carbonyl conjugated systems, appears to be general for carbonyl-conjugated radicals and to increase with the "alternating tendency" of the monomer from which the attacking radical is derived.

This lends much support to the suggestion made earlier[1a] that the driving force for "alternation" arises from the presence of resonance structures in the transition state similar to those of molecular compounds.

Possible structures of such forms, in which an electron has been transferred from styrene monomer to attacking radical, were suggested previously,[1a] but it should be pointed out that similar structures may be drawn to explain as well the great reactivity of carbonyl conjugated double bonds with styrene type radicals, and thus to account for both "halves" of the alternating copolymerization reaction.





Further, it should be noted that relative reactivities of all α-methylstyrenes toward the maleic anhydride type radical now show little relation to the Hammett sigma values of the substituents, again indicating the dominant importance of special resonance forms in the transition state of this reaction, rather than some general property of electron density or availability at the double bond, as required by any "electrostatic" interpretation.[5]

The parallel drawn between the transition state of polymerization and molecular compound formation again brings up the possibility that alternation in copolymerization may actually involve attack of a radical on a molecular complex, particularly in a pair such as styrene–maleic anhydride where appreciable concentrations of actual colored complex exist. It should be pointed out, however, that by the interpretation given above the transition from a weakly alternating system such as styrene–methyl methacrylate where participation of such a complex can be excluded[16,17] to a strongly alternating system where its role is equivocal[16] becomes one in degree, not in kind. Thus, while participation of an actual complex in the reaction would still be of importance in the over-all reaction kinetics, it would not be in our understanding of the nature of the reaction.

Summary

1. The relative reactivity of eight *meta-* and *para-* substituted α-methylstyrenes toward the maleic anhydride type radical have been determined.

2. Further evidence has been obtained that the major driving force leading to alternation in copolymerization is the presence in the transition state of polar resonance forms resembling those in the colored "molecular complexes."

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[16] Nozaki, *J. Polymer Sci.*, **1**, 445 (1946).

[17] Lewis, unpublished work in this Laboratory.