[CONTRIBUTION NO. 73 FROM THE GENERAL LABORATORIES OF THE UNITED STATES RUBBER COMPANY]

Copolymerization. XI. Copolymerizations Involving α-Vinylpyridine, α-Vinylthiophene, o-Chlorostyrene and α-Methylstyrene

BY CHEVES WALLING, EMORENE R. BRIGGS[1a] AND KATHERINE B. WOLFSTIRN[1b]

In the preceding paper of this series,[2] the copolymerization of styrene and methyl methacrylate with a series of *meta* and *para*-substituted styrenes was reported. At the same time it appeared of interest to investigate the copolymerization of these same two monomers with some other vinyl aromatics which were available.

This paper describes the copolymerization of styrene with α-vinylpyridine, α-vinylthiophene, and *o*-chlorostyrene and of methyl methacrylate with α-vinylpyridine, *o*-chlorostyrene, and α-methylstyrene. The series is not complete since it did not appear possible to analyze a styrene–α-methylstyrene copolymer accurately, and insufficient α-vinylthiophene was available for further experiments.

Due to space limitations, the ultimate experimental data on the systems have been omitted, but are available from the American Documentation Institute.[3] An idea of the accuracy of the work can, however, be gained from the graphical solutions of the copolymerization equation[4] illustrated in Figs. 1 and 2. Experimental errors (represented by the parallelograms around each intersection in the Figs.) have been calculated assuming analytical errors of 0.2% C, 0.1% N and 0.1% Cl as described previously.[5] Since all the lines corresponding to individual experiments pass through the parallelograms, the precision of the experiments may be seen to be appreciably greater than their assumed accuracy.

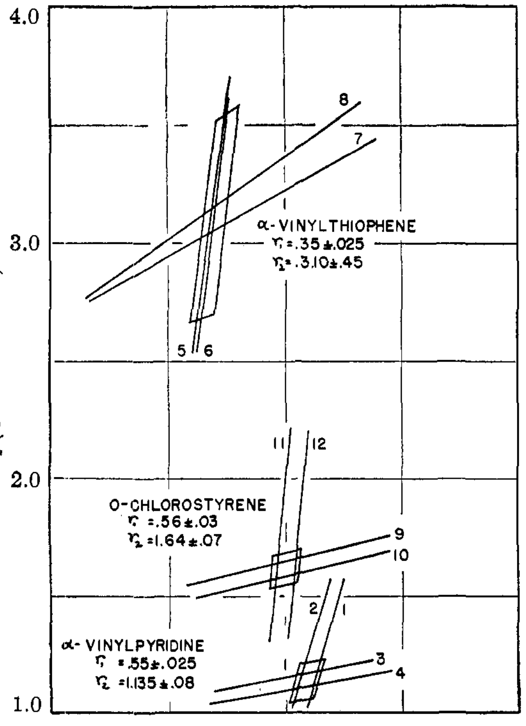

Fig. 1.—Determination of monomer reactivity ratios for some copolymerizations of styrene.

In Table I the relative reactivities towards the styrene and methyl methacrylate type radicals of the monomers are listed compared with styrene,[6]

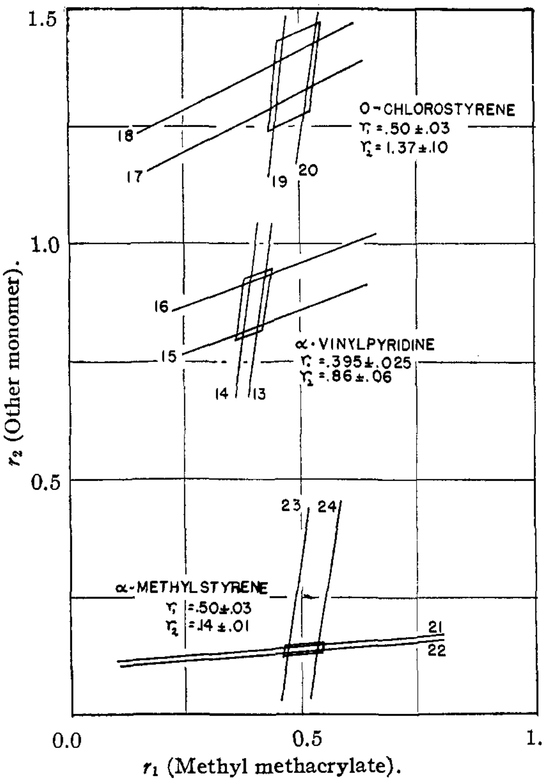

Fig. 2.—Determination of monomer reactivity ratios for some copolymerizations of methyl methacrylate.

(1a) Present address, R. F. D. 2, Guilford, Conn.

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

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

(3) Remit 50¢ for microfilm or 70¢ for photoprints of Document 2497 to American Documentation Institute, 1719 N Street, N. W., Washington 6, D. C.

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

(5) Lewis, Walling, Cummings, Briggs and Mayo, *ibid.*, **70**, 1527 (1948).

(6) *i. e.*, $1/r_1$'s for the styrene radical and $0.46/r_1$'s for the methacrylate radical, since the best value for the monomer reactivity ratio for styrene with the methacrylate radical has been found to be 0.46.[4,5]

TABLE I

RELATIVE REACTIVITIES AND MONOMER REACTIVITY RATIO PRODUCTS (r_1r_2)

Monomer	Relative reactivities toward Styrene radical	Relative reactivities toward Methacrylate radical	(r_1r_2) With styrene	(r_1r_2) 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).

PASSAIC, NEW JERSEY RECEIVED JULY 22, 1947

[CONTRIBUTION NO. 74 FROM THE GENERAL LABORATORIES OF THE UNITED STATES RUBBER COMPANY]

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).