

## Substituent Effects in Free Radical Copolymerization of Substituted Styrenes with Acrylates and Methacrylates

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### Synopsis

Relative reactivity ratios have been determined for *o*-chlorostyrene with five lower acrylates and methacrylates, respectively, and for methyl acrylate with a number of substituted styrenes in free-radical copolymerization. Analysis of the data shows that: (a) acrylates are less reactive than methacrylates with *o*-chlorostyrene; (b) length of the side chain has little or no effect in methacrylates, but its effect is pronounced in acrylates with respect to their reactivity ratios; (c) chlorine substitution in the side chain of either acrylates or methacrylates has a significant influence on the reactivity ratio; (d) relative reactivity ratio data for methyl acrylate with substituted styrenes fail to show the expected relationship between monomer structure and resonance theory, inductive effect and, consequently, the Hammett  $\sigma$  values.

### INTRODUCTION

Since Walling et al.<sup>1</sup> published their work on the effect of *meta* and *para* substituents on the relative reactivity of the styrene double bond in copolymerization, a number of publications have appeared in which substituent effect either could or could not be correlated with Hammett's  $\sigma$  values.

Other authors<sup>2-4</sup> have attempted to give a theoretical basis to the well-known  $Q$  and  $e$  scheme, even though its originators<sup>5</sup> cautioned that this was strictly an empirical formula. Indeed, in many cases calculated  $Q$  and  $e$  values do not agree with literature data, or, conversely, relative reactivity ratios calculated from published  $Q$  and  $e$  values do not agree with experi-

TABLE I  
Calculated versus Experimental Reactivity Ratio Data,  
 $M_1 = o$ -Chlorostyrene

Acrylate $M_2$	$Q_1^a$	$e_1^a$	$Q_2^a$	$e_2^a$	$r_1$		$r_2$	
					Calcd	Found	Calcd	Found
Methyl	1.28	-0.36	0.42	0.60	2.16	6	0.184	0
Ethyl	1.28	-0.36	0.52	0.22	2.00	3.89	0.358	0
<i>n</i> -Butyl	1.28	-0.36	0.50	1.06	1.535	2.19	0.087	0.17
2-Ethylhexyl	1.28	-0.36	0.41	0.39	2.38	2.77	0.239	0.21

<sup>a</sup> From Young's Tables.<sup>10</sup>

mental data (Table I). In short, no complete explanation has been offered for substituent effects in binary, free-radical copolymerization; therefore, one cannot predict with reasonable certainty the course of polymerization or the structure of the final product. In this paper we report experimental relative reactivity ratios involving monosubstituted styrenes as one of the two comonomers and conclusions that can be drawn from them. In a future publication we hope to discuss the substituent effect on a more theoretical basis as more data become available.

## EXPERIMENTAL

### Copolymerization of *o*-Chlorostyrene with Five Lower Acrylates and Methacrylates

**Monomers.** The monomers were commercially available materials. The monomers used and the sources are listed in Table II. The suppliers listed are not necessarily the sole distributors. Purification was by washing and distillation; pure monomers were stored in crown-capped bottles under nitrogen in a deep freeze. Monomer purity was checked by gas chromatography, refractive index, and infrared spectroscopy.

TABLE II

Monomer	Source
<i>o</i> -Methylstyrene	Columbia Organic Chemical Co.
<i>m</i> -Methylstyrene	Columbia Organic Chemical Co.
<i>p</i> -Methylstyrene	Monomer Polymer Laboratory
<i>p</i> -Methoxystyrene	Monomer Polymer Laboratory
<i>o</i> -Chlorostyrene	Dow Chemical Company
<i>m</i> -Chlorostyrene	Monomer Polymer Laboratory
<i>p</i> -Chlorostyrene	Monomer Polymer Laboratory
<i>o</i> -Bromostyrene	Columbia Organic Chemical Co.
<i>p</i> -Bromostyrene	Monomer Polymer Laboratory
<i>o</i> -Fluorostyrene	Chemical Procurement Laboratory
<i>p</i> -Fluorostyrene	Chemical Procurement Laboratory
Methyl acrylate	Rohm and Haas Company
Ethyl acrylate	Rohm and Haas Company
<i>n</i> -Butyl acrylate	Rohm and Haas Company
2-Ethylhexyl acrylate	Rohm and Haas Company
2-Chloroethyl acrylate	Monomer Polymer Laboratory
Methyl methacrylate	Rohm and Haas Company
Ethyl methacrylate	Rohm and Haas Company
<i>n</i> -Butyl methacrylate	Rohm and Haas Company
2-Ethylhexyl methacrylate	Monomer Polymer Laboratory
2-Chloroethyl methacrylate	Monomer Polymer Laboratory

**Polymerization.** *o*-Chlorostyrene was copolymerized by standard polymerization technique in mass, solvent, and emulsion systems. Comonomer feed compositions were changed in 10 mol-% increments, resulting in nine comonomer feed compositions containing 10–90 mole-% *o*-chlorostyrene.

for each system studied. Copolymerizations were allowed to proceed to 4% conversions.

The relative reactivity ratios are listed in Tables III and IV. Typical polymerizations are given below.

**Bulk Polymerization of 40 mole-% *o*-Chlorostyrene and 60 Mole-% Methyl Acrylate.** In a 100-cc polymerization tube were placed 25 g of a solution of 55.4 g (40 mole-%) of *o*-chlorostyrene and 51.6 g (60 mole-%) of methyl acrylate with 0.0025 g of benzoyl peroxide. The tube was flushed with nitrogen for 30 sec, sealed, and placed in a constant-temperature bath at 60°C. The onset of polymerization was determined by shaking the tube and observing the viscosity as indicated by the speed of the rising

TABLE III  
Reactivity Ratios for *o*-Chlorostyrene ( $M_1$ ) with Acrylates ( $M_2$ ),  $T = 40^\circ\text{C}$

$M_2$	Mass		Solution		Emulsion	
	$r_1$	$r_2$	$r_1$	$r_2$	$r_1$	$r_2$
Methyl acrylate	5.9 $\pm 0.27$	0.059 $\pm 0.04$	5.94 $\pm 0.37$	0 $\pm 0.03$	6 $\pm 0.43$	0 $\pm 0.03$
Ethyl acrylate	3.73 $\pm 0.035$	0 $\pm 0.06$	3.94 $\pm 0.035$	0 $\pm 0.06$	4.01 $\pm 0.43$	0.048 $\pm 0.05$
<i>n</i> -Butyl acrylate	2.10 $\pm 0.15$	0.16 $\pm 0.03$	2.13 $\pm 0.04$	0.16 $\pm 0.005$	2.25 $\pm 0.20$	0.2 $\pm 0.05$
2-Ethylhexyl acrylate	2.77 $\pm 0.15$	0.24 $\pm 0.08$	2.77 $\pm 0.03$	0.21 $\pm 0.08$	2.65 $\pm 0.23$	0.17 $\pm 0.10$
2-Chloroethyl acrylate	—	—	—	—	1.71 $\pm 0.08$	0.533 $\pm 0.015$

gas bubbles. As soon as any increase in viscosity was noted, the tube was opened and the contents poured into methanol. The precipitated polymer was redissolved in chloroform, precipitated three times, and dried to constant weight. If the yield of polymer indicated more than 4% conversion, the experiment was repeated until yields of 4% or less were obtained.

**Solvent Polymerizations.** These were run in benzene with a monomer:solvent ratio of 1:3. Polymerization progress estimation and purification were the same as in the bulk polymerization.

**Emulsion Polymerization of 40 mole-% *o*-Chlorostyrene and 60 mole-% Methyl Acrylate.** In a 100-ml beverage bottle were placed 20 g of a mixture of 55.4 g (40 mole-%) of *o*-chlorostyrene and 51.6 g (60 mole-%) of methyl acrylate with 80 ml distilled water, 1 g (5 wt %) Duponol Me (polymerization grade), 0.1 g  $\text{K}_2\text{S}_2\text{O}_8$ , and 0.05 g  $\text{K}_2\text{S}_2\text{O}_5$ . The bottle was flushed with nitrogen, capped, and tumbled in a 40°C constant-temperature bath. Within 15 min, polymerization started, as indicated by the appearance of a bluish tint and the disappearance of foam. The bottle was opened and the contents were poured into methanol. Purification was the same as described above.

TABLE IV  
Reactivity Ratios for *o*-Chlorostyrene ( $M_1$ ) with Methacrylates ( $M_2$ ),  $T = 40^\circ\text{C}$

$M_2$	Mass		Solution		Emulsion	
	$r_1$	$r_2$	$r_1$	$r_2$	$r_1$	$r_2$
Methyl methacrylate <sup>a</sup>	1.29 $\pm 0.165$	0.413 $\pm 0.15$	1.31 $\pm 0.01$	0.53 $\pm 0.075$	1.34 $\pm 0.01$	0.46 $\pm 0.075$
Ethyl methacrylate	1.40 $\pm 0.035$	0.457 $\pm 0.05$	1.31 $\pm 0.017$	0.475 $\pm 0.0325$	1.34 $\pm 0.032$	0.45 $\pm 0.03$
<i>n</i> -Butyl methacrylate	1.30 $\pm 0.33$	0.352 $\pm 0.12$	1.25 $\pm 0.33$	0.335 $\pm 0.11$	1.24 $\pm 0.33$	0.324 $\pm 0.11$
2-Ethylhexyl methacrylate	2.8 $\pm 0.23$	0.425 $\pm 0.08$	2.74 $\pm 0.04$	0.394 $\pm 0.09$	2.74 $\pm 0.04$	0.394 $\pm 0.09$
2-Chloroethyl methacrylate	—	—	—	—	0.909 $\pm 0.005$	0.885 $\pm 0.107$

<sup>a</sup> Literature:<sup>1</sup>  $r_1 = 1.37 \pm 0.1$ ;  $r_2 = 0.50 \pm 0.03$  at  $60^\circ\text{C}$ .

Water solubilities of the various monomers were measured (Tables V and VI). No correlation exists between reactivity ratio data and the water solubility, an observation supported by the fact that relative reactivity ratios for a given pair of monomers are practically identical for mass, solvent, and emulsion polymerization.

The only instance where water solubility exerts an effect is in the reaction rate. Systems having a high content of relatively water-soluble monomer polymerize faster than those having a low content in an emulsion system as indicated by the exotherm (Fig. 1). Exotherms were measured internally in the polymerization media with a thermocouple connected to a recorder.

TABLE V  
Water Solubility of Acrylates at 40°C

Monomer	Solubility, g/100 ml
<i>o</i> -Chlorostyrene	0.0046
Methyl acrylate	5.09
Ethyl acrylate	1.60
<i>n</i> -Butyl acrylate	0.151
2-Ethylhexyl acrylate	0.014

TABLE VI  
Water Solubility of Methacrylates at 40°C

Monomer	Solubility, g/100 ml
<i>o</i> -Chlorostyrene	0.0046
Methyl methacrylate	0.468
Ethyl methacrylate	0.118
<i>n</i> -Butyl methacrylate	0.016
2-Ethylhexyl methacrylate	0.017

Although the heat of polymerization of methyl acrylate (18.8 kcal/mole) is 2.7 kcal/mole more than that of *o*-chlorostyrene (16.08 kcal/mole), we do not believe that the exotherm can be attributed solely to this energy difference; therefore water solubility, i.e., the rate of diffusion, plays a major role.

**Reactivity Ratio Determinations.** For the determination of the *o*-chlorostyrene content of the copolymers, a calibration curve was plotted for the intensity of ultraviolet absorption of various concentrations of poly-*o*-chlorostyrene in the copolymers. A family of absorption curves is shown in Figure 2. From the calculated curve it was then possible, at a known concentration (0.1500 g/250 ml of chloroform) of copolymer, to ascertain the percentage of *o*-chlorostyrene in the unknown.<sup>6,7</sup>

Data were then tabulated in the manner of the Fineman-Ross plotting form,<sup>8</sup> the slope and intercept of the curves being determined by a least-squares analysis of the data.

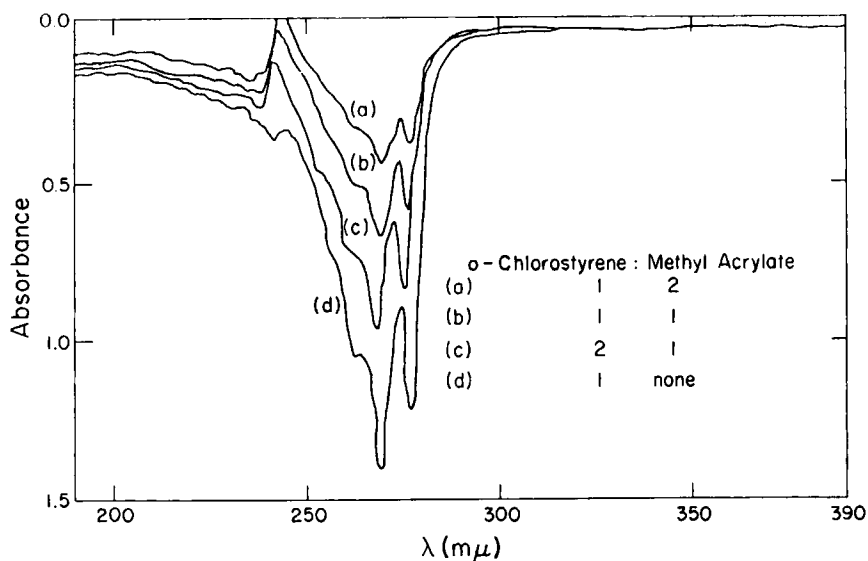
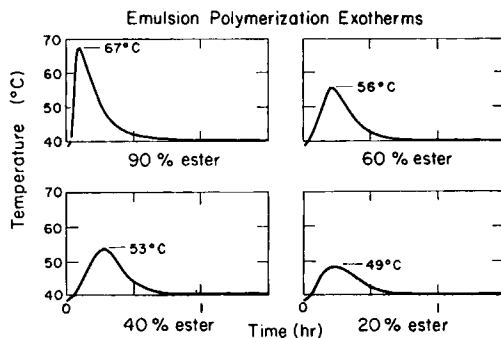
Fig. 1. *o*-Chlorostyrene absorbance curves.

Fig. 2. Emulsion polymerization exotherms.

### Copolymerization of Methyl Acrylate with Substituted Styrenes

All monomers are commercially available except *o*-methoxystyrene, which was prepared as described elsewhere.<sup>9</sup>

The purity of the monomers was checked by gas chromatography, refractive index, and infrared spectroscopy.

Polymerization technique and relative reactivity ratio determinations are identical with those given above. In Table VII are given the relative reactivities, where  $M_1$  is substituted styrene and  $M_2$  is methyl acrylate.

TABLE VII  
Relative Reactivity Ratios of Substituted Styrene  
and Methyl Acrylate ( $M_2$ )

Substituent on styrene ( $M_1$ )	$r_1$	$r_2$
—	0.75	0.2
<i>o</i> -Me	0.98	0.27
<i>p</i> -Me	1.65	0.14
<i>p</i> -Me	1.54	0.17
<i>o</i> -Me()	2.6	0.04
<i>p</i> -Me()	2.0	0.07
<i>o</i> -F	3.8	0.01
<i>p</i> -F	2.6	0.04
<i>o</i> -Cl	6	0.002
<i>p</i> -Cl	4.8	0.002
<i>p</i> -Cl	3.9	0.01
<i>o</i> -Br	6.9	0
<i>p</i> -Br	6	0.01
<i>r</i> -C=N <sup>a</sup>	9.5	0

<sup>a</sup> Measured only on three points on the curve.

## DISCUSSION

Observation of the data in Tables I and III shows the apparent effect of hyperconjugation of the methyl group in the methacrylate unit upon the double bond; the length of the side chain seems to have little influence. In the series in which the acrylate esters are copolymerized with *o*-chloro-styrene, the side-chain length has a pronounced effect on the relative reactivity ratio. We are at a loss to explain this, but it does show how minor structural differences in a monomer and/or radical can profoundly change its behavior in copolymerization. This is also observed in both 2-chloro-ethyl esters. It is improbable that the effect of the chlorine is transmitted solely through the chain and we believe that a rather strong field effect is responsible for the enhanced reactivity of these esters. Further studies of this phenomenon are in progress.

From Table VII we can draw the following conclusions, which to us were rather startling.

(1) No matter what the substituent is, it increases the relative reactivity of the styrene moiety.

(2) The closer the substituent is to the vinyl double bond of the styrene derivative the greater the influence it exerts (except for *o*-methyl).

(3) The change in reactivity in halogen-substituted styrenes is the reverse of what one would expect from electronegativity data.

(4) The number of unshared electron pairs in a substituent is more important than the size of the substituent.

In short, the effect of a substituent on styrene in free-radical copolymerization with methyl acrylate depends, at least in part, on: (a) the dis-

tance of the substituent to the vinyl double bond; (b) the size of the substituent; and (c) the number of unshared electron pairs in the substituent.

Literature data<sup>10</sup> show that the same effects operate in the free radical copolymerization of substituted styrenes with methyl methacrylate.

The failure of these data to conform with existing resonance and inductive effect theory (and consequently Hammett's  $\sigma$  values) points up the risk inherent in attempting to apply concepts, theories and mechanisms from the field of ionic chemistry to free-radical copolymerization theory.

### References

1. C. Walling, E. R. Briggs, K. Wolfstern, and F. R. Mayo, *J. Amer. Chem. Soc.*, **70**, 1537 (1948).
2. T. C. Schwan and C. C. Price, *J. Polym. Sci.*, **40**, 457 (1959).
3. M. Chorton and A. J. Capata, *J. Polym. Sci. A*, **2**, 1321 (1964).
4. M. C. Shen, *J. Polym. Sci. B*, **1**, 11, (1963).
5. T. Alfrey, Jr., and C. C. Price, *J. Polym. Sci.*, **2**, 101 (1947).
6. H. A. Cartinen, F. A. Miller, and T. D. Parks, *J. Amer. Chem. Soc.*, **69**, 2707 (1947).
7. E. J. Meehan, *J. Polym. Sci.*, **1**, 175 (1946).
8. M. Fineman and S. D. Ross, *J. Polym. Sci.*, **5**, 259 (1950).
9. C. S. Marvel and D. Hein, *J. Amer. Chem. Soc.*, **70**, 1895 (1948).
10. G. E. Ham, *Copolymerization*, Interscience, New York, 1964.

Received November 13, 1969