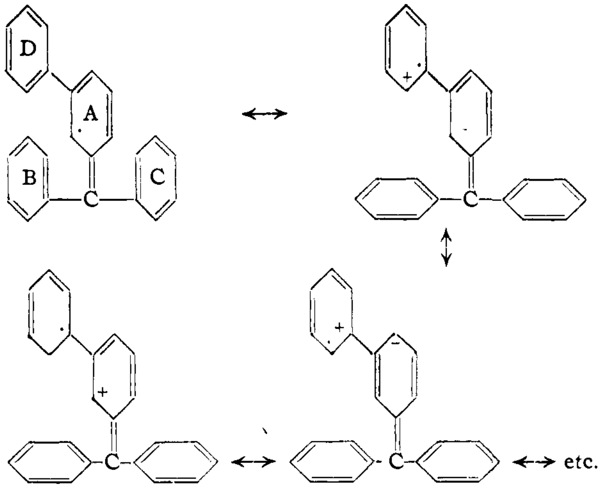

With a given charge in ring D there are 216 symbolic structures with the opposite charge in ring A,[30] the same number with the opposite charge in ring B and in ring C, respectively; with the charge on the central carbon, there are 144 contributing forms, yielding a total of 792 symbolic structures. There must be an equal number with opposite polarity, giving 1584 forms of similar stability. With a *p*-phenyl group there are an equal number of analogous dipolar contributions in addition to the 12 non-polar structures in which the odd electron is distributed into the *o*- and *p*-positions of the *p*-phenyl group. The evidence that one *m*-phenyl has an only slightly smaller influence than one *p*-phenyl indicates that the dipolar forms contribute significantly to the radical.

There is some evidence indicating that dipolar contributions are more important in free radicals than in molecules with no odd electrons. Thus the dipole moment of 1-picryl-2,2-diphenylhydrazyl radical (4.92 *D*) is appreciably greater than that of the corresponding hydrazine (3.59 *D*).[31] It has been suggested[32] that this is due to dipolar contributions being more important in the free radical. Importance has also been ascribed to dipolar contributions to the activated complexes for free radical copolymerizations where the alternating effect is dominant.[33]

The present treatment would not seem capable of fully explaining the report[14,28,29] that hexa-*m*-biphenylylethane is considerably more highly dissociated than hexa-*p*-biphenylylethane. It has been suggested[34] that Pascal's constants are not accurate when applied to estimation of the diamagnetic susceptibility of a free radical and that the hexa-*p*-substituted compound is completely dissociated in solution. This conclusion may apply equally well to the meta isomer. Although this throws doubt on the accuracy of the dissociation constants for the *sym*-bis-biphenylyltetraphenylethanes, there can be little question that they are of comparable magnitudes.

Acknowledgment.—The authors gratefully acknowledge a Frederick Gardner Cottrell Grant from the Research Corporation which made this work possible.

[30] These calculations take into account Kekulé resonance; *e.g.*, in rings B and C in this case.

[31] J. Turkevich, P. F. Oesper and C. P. Smyth, THIS JOURNAL, **64**, 1179 (1942).

[32] Ref. 5, p. 198.

[33] F. R. Mayo and C. Walling, *Chem. Revs.*, **46**, 244 (1950).

[34] P. W. Selwood and R. M. Dobres, THIS JOURNAL, **72**, 3860 (1950).

BOSTON, MASS. RECEIVED MAY 17, 1951

[CONTRIBUTION FROM THE INSTITUTE OF POLYMER RESEARCH, POLYTECHNIC INSTITUTE OF BROOKLYN]

Ionic Copolymerization. The Effect of Reaction Conditions on the Monomer Reactivity Ratios for the System Styrene–*p*-Chlorostyrene–Stannic Chloride

BY C. G. OVERBERGER, LESTER H. ARNOLD AND JOHN J. TAYLOR

This work was undertaken in order to study the effect of reaction variables on the monomer reactivity ratios of a typical copolymer system catalyzed by a cationic catalyst. Such data were not available but are very necessary before additional quantitative or semi-quantitative copolymerization data obtained with cationic catalysts, can be interpreted. In the system styrene, *p*-chlorostyrene, stannic chloride; we have demonstrated that: (1) an actual copolymer is probably obtained; (2) the effect of dielectric constant on the monomer reactivity ratios is small. With a range of dielectric constants from approximately 2.2 to 29.7, the effect is smaller than the accuracy of the chlorine determinations; (3) the effect of known, small amounts of water on the monomer reactivity ratios is small; (4) the effect of catalyst concentration on the monomer reactivity ratios for the system *p*-chlorostyrene-α-methylstyrene is negligible; (5) the reactivity ratios determined at 30°, 0° and −20° for the styrene–*p*-chlorostyrene system are not appreciably different.

Since the development of the copolymer composition equation,[1] a large amount of copolymerization data has been obtained in the form of reactivity ratios. For the most part, these data[2] have been obtained for radical-catalyzed copolymerizations. Within the past five years, a number of copolymer systems have been described catalyzed by cationic catalysts. Most of these data have usually consisted of one experiment with a 50–50 monomer mixture. For the most part, these data have satisfied the intention, namely, as a diagnostic test for determining the mechanism of polymerization with free-radical and ionic catalysts.[3] On examination of the literature, one is aware, however, of the sparsity of any quantitative or even semi-quantitative data[4] available for cationic-catalyzed copolymerization. It is the purpose of this paper and succeeding ones to obtain such information.

The determination of relative reactivities of

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[1] (a) T. Alfrey and G. Goldfinger, *J. Chem. Phys.*, **12**, 205 (1944); (b) F. R. Mayo and F. M. Lewis, THIS JOURNAL, **66**, 1594 (1944); (c) F. T. Wall, *ibid.*, **66**, 2050 (1944).

[2] F. R. Mayo and C. Walling, *Chem. Revs.*, **46**, 191 (1950).

[3] C. Walling, E. R. Briggs, W. Cummings and F. R. Mayo, THIS JOURNAL, **72**, 48 (1950).

[4] For notable exceptions, see Table 18, reference 2.

vinyl monomers with ionic catalysts presents new and interesting problems not encountered in the determination of relative reactivities of monomers in free radical copolymerization. Furthermore, few data are available concerning the structure of polymers or copolymers prepared by cationic catalysts. Reactivity ratios reported for copolymer systems calculated from one or two monomer compositions are subject to some doubt because there is always the possibility that an actual copolymer was not obtained. Since ions or ion pairs are involved, the effect of the dielectric constant of the solvent and the effect of temperature on the monomer reactivity ratios needed clarification. The effect of catalyst concentration and the nature of the catalyst on the reactivity ratios is as yet undetermined. Florin[5] has studied the effect of different catalysts on the values of r_1 and r_2 for the monomer pair; styrene–3,4-dichlorostyrene. His results indicate that r_1 and r_2 vary with the strength of the catalyst, the stronger acids causing the dichlorostyrene monomer to be more reactive with a styrene carbonium ion and the weaker acids causing it to be less reactive (see later section).

Our limited objective (described in paper II of this series) was the copolymerization of styrene and *p*-chlorostyrene with other meta- and para-substituted styrenes in order to see whether the data could be correlated with the σ and ρ constants of Hammett.[6] An initial determination of the effect of the variables presented above was important in order to be able to critically evaluate further copolymerization data.

This paper reports the effect of reaction conditions on the monomer reactivity ratios for the system styrene–*p*-chlorostyrene catalyzed by stannic chloride. Some data are also presented for the system *p*-chlorostyrene–α-methylstyrene.

Experimental

Monomers.—A commercial sample of styrene was washed three times with 5% sodium hydroxide followed by several washings with distilled water. The styrene was then dried over magnesium sulfate and fractionally distilled under reduced pressure.

α-Methylstyrene (Dow) was distilled under reduced pressure, b.p. 50° (8 mm.), $n^{25}\text{D}$ 1.5357. Sabetay[7] reported a b.p. of 159–160° (44 mm.), $n^{22}\text{D}$ 1.5350.

p-Chlorostyrene was prepared by the addition of methylmagnesium iodide to *p*-chlorobenzaldehyde according to a general procedure referred to in reference 8, followed by hydrolysis of the addition product and dehydration of the carbinol, b.p. 38° (2 mm.), $n^{25}\text{D}$ 1.5604 (38–39° 2 mm., $n^{20}\text{D}$ 1.5648).[9]

Purification of Catalyst.—C.P. stannic chloride was heated under reflux with phosphorus pentoxide in an all glass apparatus for one hour. A calcium chloride drying tube was employed to protect the stannic chloride from moisture. The stannic chloride was then cooled, the drying tube removed, and the apparatus adjusted for distillation.[10] Small capillary lengths of varying capacity were drawn very fine at both ends and sealed off at one end. They were weighed and assorted according to their dimensions. The procedure for filling was as follows. Five ampules, open ends down, were placed in a large test-tube having a side-arm. The latter was then used as a receiver in a stannic chloride distillation set-up. The side-arm of the test-tube was attached to a two-way stopcock, one arm of which led to a vacuum pump (protected by alkaline and Dry Ice traps), and the other, through a drying agent, to the atmosphere. The adapter connecting the condenser and receiver was equipped with a stopcock so that the receiver could be removed without allowing the atmosphere to come into contact with the stannic chloride. To fill the ampules, the distilling flask was heated and vacuum applied until about 5 ml. of stannic chloride distilled over. The adapter stopcock and the two-way stopcock were both turned so that the pressure of the atmosphere forced the stannic chloride into the ampules. The receiver was then quickly disconnected, the excess stannic chloride discarded, and the ampules sealed in a hot flame. The filled ampules were cleaned, dried and weighed.

Solvents.—Carbon tetrachloride, C.P., was dried over magnesium sulfate and then fractionally distilled; b.p. 76.5° (atm.), $n^{26}\text{D}$ 1.4570.

Nitrobenzene, C.P., was washed with sulfuric acid (1:1), water, 10% sodium hydroxide (until the aqueous layer was colorless), and finally water (until alkali free). It was then dried over anhydrous calcium sulfate and activated alumina and fractionally distilled under reduced pressure, the first and last 20% portions being discarded.

Polymerization Technique.—The apparatus[11] consisted of a medical hypodermic syringe equipped with a stopcock and needles of varying lengths. The stopcock and needles were of stainless steel. Four- and one-ounce screw-cap bottles were used for the polymerization mixtures. Small holes were drilled in the caps to allow passage of the needle. Two small rubber circles, one of self-sealing butyl rubber and the other of an insoluble polyvinyl chloride–Hycar composition were placed in the cap, the butyl rubber being next to the top of the cap. This type of cap has been described by Houston.[12] The bottles were cleaned with cleaning solution, rinsed with water, followed by acetone, and placed in a 115° oven. To remove as much moisture as possible from the surfaces of the bottles, they were taken from the oven and placed in a vacuum desiccator, which was evacuated while the bottles were still hot. After a short time, the desiccator was filled with nitrogen and the bottles capped while they were still in the nitrogen atmosphere. An alternative procedure, used in the later experiments, consisted of placing the bottles on a manifold, evacuating them by means of a pump, heating them cautiously by means of a hot flame (while still under vacuum), and finally charging them in a dry box through which dry nitrogen was passed.

The bottles were weighed and then charged with monomers and solvent. The weight of each constituent was obtained by difference. After charging, the caps were screwed on the bottles which were then placed in a 0° ice-bath.

The catalyst solution was prepared as follows. A screw-cap bottle was filled with a definite volume of solvent, depending on the desired total amount and concentration of the catalyst solution. An ampule containing a known amount of stannic chloride was introduced into the bottle. At the same time a stream of dry nitrogen was led into the mouth of the bottle to prevent the entrance of moisture. The ampule was broken under the surface of the solvent by tapping with a glass rod. The bottle was then quickly capped.

In the experiments where the effect of cocatalyst was studied, the catalyst solutions were prepared in the following manner. The anhydrous stannic chloride solutions were made as described. Ampules were filled with desired quantities of water. The water was added to the catalyst solution by inserting an opened capillary end of a water

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[5] R. E. Florin, This Journal, **73**, 4468 (1951).

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

[7] S. Sabetay, *Bull. soc. chim.*, [4] **47**, 614 (1930).

[8] C. G. Overberger and J. H. Saunders, "Organic Syntheses," Vol. 28, John Wiley and Sons, Inc., New York, N. Y., p. 31.

[9] C. S. Marvel and G. L. Shertz, This Journal, **65**, 2054 (1943).

[10] A modification of the described technique was used for the initial work in the system α-methylstyrene–*p*-chlorostyrene. For brevity the procedure has been omitted. The results obtained with both procedures were identical.

[11] A different technique was employed initially with the α-methylstyrene–*p*-chlorostyrene system. For the sake of brevity these details are omitted. It should be emphasized, however, that the technique was a very accurate one, but more tedious than the one described in detail.

[12] R. J. Houston, *Anal. Chem.*, **20**, 49 (1948). We are indebted to Mr. E. A. Willson of the B. F. Goodrich Company for a generous supply of these rubber sheets.

ampule through one of the holes in the bottle cap (made by first inserting and withdrawing a hypodermic needle) and then carefully vaporizing the water out of the ampule by means of the flame of a microburner. In this way it was hoped to avoid local excesses of water. The catalyst-cocatalyst solutions were allowed to stand for at least one hour, with intermittent shaking, before being used in a polymerization experiment.

The syringe was flushed with nitrogen to remove water vapor. An aliquot portion of catalyst solution was drawn up into the syringe and injected into a reaction mixture. The bottle containing the latter was then quickly weighed, and replaced in the ice-bath. The syringe was cleaned by rinsing with methanol, followed by ether and then dried. Conversion was estimated by the amount of precipitate obtained when 0.5 to 1 ml. of reaction mixture (removed by syringe) was added to a test-tube containing methanol. When the degree of conversion was judged to be around 10% or less, the reaction bottle was uncapped and a measured amount (around 1 ml., accurately weighed) added to methanol in an erlenmeyer flask in order to determine the exact conversion by bromine titration. (This method of determining conversion was not employed in the system α-methylstyrene–p-chlorostyrene.) The remaining solution was then poured into several volumes of methanol and the polymer purified by three successive solutions in methyl ethyl ketone and reprecipitations in methanol.

Estimation of Conversion.—Because of the fact that acid-catalyzed polymerizations yield low molecular weight products at 0°, it was thought desirable, during the course of these studies, to determine conversion by titration of the residual monomers at the time of precipitation. The method used was that described by Uhrig and Levin[13] and consists of titration with a 2% solution of bromine in glacial acetic acid. The bromine solution is standardized by titration of pure styrene. For the system styrene–p-chlorostyrene the method is fairly reliable; for styrene monomers containing electron withdrawing groups the method is unreliable due to slow rates of bromine addition.

Results and Discussion

I. Fractionation of a Copolymer of Styrene and *p*-Chlorostyrene.—A good experimental fit of sufficient data to the copolymer composition equation is an indication that a copolymer has probably been obtained. As further verification, a polymer from a (75) styrene–(25) p-chlorostyrene monomer mixture was fractionated into seven fractions by precipitation from methyl ethyl ketone solution by methanol. The results are shown in Table I. The reasonable uniformity of the fractions strongly indicates the formation of a copolymer.

TABLE I

FRACTIONATION OF A COPOLYMER OF STYRENE (M_1) AND p-CHLOROSTYRENE[a] (M_2)

	Polymer composition	
Fractions	Cl,[b] %	Mole, % m_2
A	3.99	12.20
B	4.24	12.93
C	4.13	12.82
D	4.28	13.10
E	4.18	12.83
F	4.35	13.35
G	4.55	14.10

[a] Prepared at 0°, 50–50 carbon tetrachloride–nitrobenzene mixture, 1.0% stannic chloride, mole % of M_2 in monomer 24.42, reaction time, 0.13 hr., conversion, 15.22%. [b] Analyses by Dr. K. Ritter, Zurich, Switzerland.

II. Effect of Dielectric Constant.—It has been established that the higher the dielectric constant of the medium at any given temperature, the faster will be the over-all rate[14] of a cationic-catalyzed polymerization. A number of questions initially suggest themselves. Does the anion from the cocatalyst[15] which is part of the ion pair in the growing carbonium ion affect the reactivity of the carbonium ion; if so, is the separation of ions important and is the nature of the anion important? (See reference 20; see also F. R. Mayo and C. Walling, THIS JOURNAL, **71**, 3845 (1949) for an interpretation of the nature of the growing ion pair.) These questions cannot be answered unequivocally from a determination of monomer reactivity ratios since only relative reactivities of carbonium ions can be determined. From the data of Table II, however, it is apparent that with a given anion derived from a cocatalyst [$SnCl_4 \cdot xH_2O$], the polymer composition does not change appreciably in a (75) styrene–(25) p-chlorostyrene initial monomer mixture as the dielectric constant is changed from *ca.* 2.2 to 29.7. From the data of Table III, it can be seen that the system styrene–p-chlorostyrene in carbon tetrachloride–nitrobenzene (1:1) at 0° gave r_1, 2.10 ± 0.2; r_2, 0.35 ± 0.02 and in carbon tetrachloride at 0°, r_1, 2.5 ± 0.4; r_2, 0.30 ± 0.03,[16] Fig. 1. Thus, there does not appear to be an appreciable change in the relative reactivities of the carbonium ions in this one system.

TABLE II

EFFECT OF DIELECTRIC CONSTANT ON POLYMER COMPOSITION

Dielectric constant[a]	p-Chlorostyrene in monomers,[b] %	Cl in polymer, %	
2.2	25.4	4.64	
2.2	25.0	4.90	
2.2	25.2	4.63	
2.2	25.6	5.13	
7.5	25.9	4.27	
14.0	24.9	4.46 4.65	dupl.
14.0	25.1	4.61 4.77	dupl.
14.0	25.3	4.81	
14.0	25.6	4.35	
29.7	25.5	4.17	
29.7	25.8	5.07	

[a] The values of 2.2, 7.5, 14.0 and 29.7 correspond, respectively, to the following solvent compositions: carbon tetrachloride, o-dichlorobenzene, carbon tetrachloride–nitrobenzene (1:1, molar), nitrobenzene. [b] All of these values are corrected for finite conversion. Except for the first run (12.2%), all conversions were under 10%.

Price and Walsh[17] have recently reported supporting evidence for the conclusion expressed by Walling and Mayo[18] that strong polar effects in radical catalyzed copolymerizations are not detectable by changing the dielectric constant of the medium.[19] From consideration of the model of

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(13) K. Uhrig and H. Levin, *Ind. Eng. Chem., Anal. Ed.*, **13**, 90 (1941).

(14) D. C. Pepper, *Nature*, **158**, 789 (1946).

(15) It is almost completely accepted that a cocatalyst is necessary for cationic-catalyzed polymerization: see (a) A. G. Evans and G. W. Meadows, *J. Polymer Sci.*, **4**, 359 (1949); (b) H. Plesch, M. Polanyi, H. A. Skinner and M. A. Weinberger, *Nature*, **157**, 102 (1946).

(16) Compare r_1, 2.2 ± 0.3; r_2, 0.35 ± 0.1 for the same system in carbon tetrachloride at 30°; [T. Alfrey and H. Wechsler, THIS JOURNAL, **70**, 4266 (1948)] recalculated values, see reference 2.

(17) C. C. Price and J. G. Walsh, *J. Polymer Sci.*, **6**, 239 (1951).

(18) C. Walling and F. R. Mayo, *ibid.*, **3**, 895 (1948).

(19) For a discussion of different interpretations of these data see references 15 and 16.

TABLE III

COPOLYMERIZATION OF STYRENE AND *p*-CHLOROSTYRENE AT 0°

Mole % M_2[b] in monomer mixture	Reaction time, hr.	Conversion,[c] %	Polymer composition Cl,[d] %	Polymer composition Mole m_2, %
Styrene (M_1) and *p*-Chlorostyrene (M_2)[a]				
10.7	4.5	13	1.73	5.2
40.7	9.3	7	6.22	19.4
61.9	23.3	19	10.84	35.6
69.6	23.6	18	13.82	46.9
81.0	23.5	10	17.09	60.2
88.9	35.0	8	19.94	72.6
Styrene (M_1) and *p*-Chlorostyrene (M_2)[e]				
10.92	0.07	3.3	2.44	7.38
34.00	.05	0.9	5.80	18.05
48.70	.07	1.2	8.73	28.03
58.70	.07	0.9	11.48	37.90
69.50	.17	1.0	14.18	48.30
85.50	.24	0.6	19.03	67.50

[a] In pure carbon tetrachloride as solvent; 2.0% stannic chloride based on monomers, $r_1 = 2.5 \pm 0.4$; $r_2 = 0.30 \pm 0.03$. [b] Corrected for finite conversions. [c] By bromine titration of residual monomers. [d] Chlorine analyses by Dr. K. Ritter, Zurich, Switzerland. [e] In 50–50 carbon tetrachloride–nitrobenzene mixture; 0.5% stannic chloride based on monomers, $r_1 = 2.10 \pm 0.2$; $r_2 = 0.35 \pm 0.02$.

the transition state described by Price and Walsh adapted from that of Kirkwood and Westheimer,[20] it might be predicted that even in cationic-catalyzed copolymerizations the effect of the dielectric constant of the medium on the reactivity ratios would be small provided that the effect of the anion is unimportant, an assumption which probably is not valid in some systems.

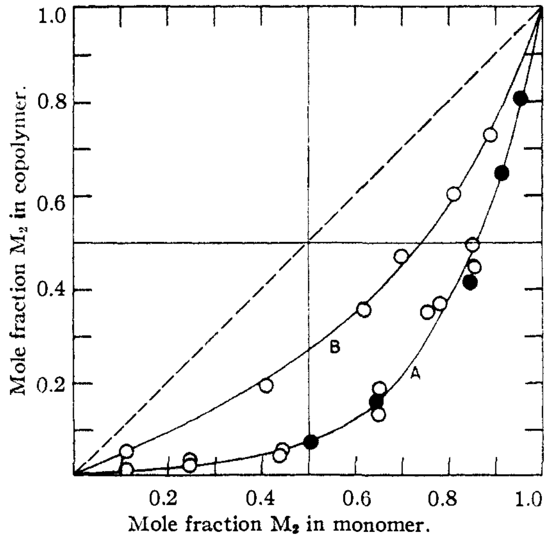

Fig. 1.—Copolymer composition curves: A, α-methylstryene (M_1); +*p*-chlorostyrene (M_2) (○, points obtained with 2.0% stannic chloride; ●, points obtained with 0.5% catalyst) in carbon tetrachloride solution at 0°; B, styrene (M_1); *p*-chlorostyrene (M_2) in carbon tetrachloride at 0°; $r_1 = 2.5 \pm 0.4$; $r_2 = 0.30 \pm 0.03$.

The effect of different catalysts on the monomer reactivity ratios has not been described in this paper. The work of Florin previously referred to, although not unequivocal, has indicated that the nature of the catalyst does affect the monomer reactivity ratios. A previous paper by Florin[21] had predicted that r_1 and r_2 would vary, depending on the catalyst, assuming the mechanism proposed by Fontana and Kidder.[22] Recent data reported by Florin[5] indicate that r_1 and r_2 vary in the system *o*-chlorostyrene–styrene with solvents of different dielectric constant using aluminum chloride as a catalyst but not with stannic chloride. These results with stannic chloride corroborate our data.

III. The Effect of Water.—If the effect of different anions from a different catalyst is important, it might be expected that the different hydrates of stannic chloride would give rise to anions of different activity ($SnCl_4OH^{\ominus}$, $SnCl_4O_2H_3^-$). An attempt to answer this question by

TABLE IV

EFFECT OF WATER CONCENTRATION ON POLYMER COMPOSITION[a]

Equivalents of water[b]	*p*-Chlorostyrene in monomers, %	Cl in[c] polymer, %	Conversion, %	Time, hr.
0	26.4	4.09	4	0.1
0	24.6	3.87	1	0.1
0	24.9	3.93	2	0.25
1	25.3	3.43	3	12.5
1	25.1	3.77	1	2.1
2	25.1	4.45	1	47.0
2	25.7	4.1	1	47.0
3	25.2		Very low	24.0

[a] In carbon tetrachloride–nitrobenzene solution (1:1); temperature 0°. Stannic chloride concentration 0.5% molar, based on monomers. [b] Based on catalyst. Crystals were noted after the catalyst solution was injected into the reaction bottle. Apparently the hydrate began to crystallize. [c] Chlorine analyses by Dr. K. Ritter, Zurich, Switzerland.

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[20] J. G. Kirkwood and F. H. Westheimer, *J. Chem. Phys.*, **6**, 506 (1938).

[21] R. B. Florin, THIS JOURNAL, **71**, 1867 (1949).

[22] C. M. Fontana and G. A. Kidder, *ibid.*, **70**, 3745 (1948). The exact mechanism of a cationic catalyzed polymerization and its kinetic interpretation is beyond the scope of this paper. According to Fontana and Kidder, the over-all rate depends on the total concentration of active center (equal to the cocatalyst 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, 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. On the other hand, Plesch [H. Plesch, *J. Chem. Soc.*, 543 (1950)] and Eley and Richards [D. D. Eley and A. W. Richards, *Trans. Faraday Soc.*, **45**, 425 (1949)] derive their kinetic expressions on the assumption of a steady-state concentration of carbonium ions. We feel that the validity of a mechanism that postulates a small steady-state concentration of carbonium ions depends on the nature of the equilibrium between catalyst and cocatalyst and secondly, on the rate constant for initiation. For a reactive catalyst (Fontana and Kidder), it is probable that the maximum carbonium ion concentration is rapidly built up. The concentration of active centers is maintained at a constant level for the greater part of the reaction (chain transfer with monomer) or falls off with time unimolecularly [if termination occurs by incorporation of cocatalyst in the chain (Plesch)].

Only in systems where, due to the weakness of the catalyst–cocatalyst system, the rate constant for initiation is not very great compared with that for termination is it possible to make the steady-state assumption. The mechanisms of Fontana and Kidder and of Mayo and Walling, on the other hand, treat the carbonium ion concentrations as equilibrium concentrations determined by ionization constants; rate constants for initiation and termination do not appear. A detailed analysis of both these possibilities will be considered in a later paper.

accurately adding known amounts of water to the polymerization system was inconclusive; at least, no major change in polymer composition could be detected (Table IV). This result could mean that there is little or no difference in the base strength of these anions derived from stannic chloride hydrate. Thus, a solubility factor may be important here. The hydrates seem to slowly crystallize from the carbon tetrachloride solution. The hydrates may be sufficiently insoluble resulting in such an unfavorable equilibrium, that the catalyst may not be available. Alternatively, the tendency of stannic chloride to form the dihydrate may be so powerful that the dihydrate may be the only effective catalyst–cocatalyst species, regardless of the water concentration. This further helps to explain why our experimental technique gave reliable duplication.

IV. Effect of Catalyst Concentration.—The effect of the stannic chloride concentration (0.5 to 2%) in the system *p*-chlorostyrene–α-methylstyrene was shown to be negligible (Table V, Fig. 1).

TABLE V

COPOLYMERIZATION OF α-METHYLSTYRENE (M_1) AND *p*-CHLOROSTYRENE (M_2)

Catalyst[a] concn., %	Mole % M_2 in monomer mixture[b]	Time, hr.	Conversion, %	Polymer composition Cl,[c] %	Mole m_2, %
2.0	10.9	0.5	16.3	0.49	1.64
2.0	24.5	.5	11.8	0.76	2.54
2.0	24.6	.5	13.6	1.00	3.34
2.0	44.0	.75	11.8	1.68	5.66
2.0	44.1	.75	13.3	1.46	5.04
2.0	64.8	2.5	5.1	3.96	13.5
2.0	85.0	1.5	6.4	13.75	49.7
2.0	65.0	1.2	2.8	5.55	19.1
2.0	64.1	1.1	2.0	4.51	15.4
2.0	77.9	1.7	15.7	10.42	37.0
2.0	75.3	1.3	6.7	10.0	35.2
2.0	85.4	1.1	3.4	12.35	44.3
0.5	49.8	1.5	3.3	2.07	7.0
.5	64.4	1.5	1.0	4.61	15.8
.5	84.6	2.2	1.0	11.55	41.2
.5	91.6	1 week	1.6	17.66	65.7
.5	95.7	1 week	0.7	21.4	81.4

[a] Based on monomers. [b] Where conversion is greater than 6%, correction has been made. [c] Analyses by E. Goldsmith, Polytechnic Institute of Brooklyn, Dr. F. Schwarzkopf, New York, N. Y., and Mr. H. S. Clark, Urbana, Illinois.

V. The Effect of Temperature.—The reactivity ratios for the system styrene–*p*-chlorostyrene were determined at 0 and −20° (Table VI). Previous data[16] were available for the same system at 30°. The results indicate only small differences in the reactivity ratios at these three temperatures. Larger temperature differences may be required, however, to successfully measure temperature coefficients. Difficulties in working in homogeneous systems at lower temperatures make this experimental problem difficult.

TABLE VI

COPOLYMERIZATION OF STYRENE (M_1) AND *p*-CHLOROSTYRENE (M_2) AT −20°[a]

Mole % M_2 in monomer mixture	Reaction time, hr.	Conversion, %	Polymer composition Cl, %	Mole m_2, %
27.50	60.8	3.3	3.10[b]	9.3
28.18	83.5	1.1	3.26[b]	9.8
28.35	112.5	0.1	3.54[b]	10.8
33.25	94.0	0.5	6.96[b]	21.9
33.85	65.0	11.8	6.87[c]	21.7
49.20	129.0	4.2	9.31[b]	30.0
49.70	129.0	1.2	9.17[b]	26.4
52.50	65.5	1.2	10.45[c]	30.0
66.20	114.5	0.5	13.55[c]	45.8
67.20	98.0	0.5	14.65[c]	50.0

[a] In 100% carbon tetrachloride, 1.0% stannic chloride. [b] Analyses by Dr. K. Ritter, Zurich, Switzerland. [c] Analyses by Drs. Weiler and Strauss, Oxford, England.

From the work of DeHaes and Smets[23] an additional set of data is now available. These authors found r_1 and r_2 for the system α-methylstyrene, *p*-chlorostyrene to be 28 ± 2 and 0.12 ± 0.03, respectively, using stannic chloride at −78°. Corresponding values obtained here for the same system at 0° are 15.5 ± 1.5 and 0.35 ± 0.05. If assumptions are made that inhomogeneity of the solution is unimportant and no solubility or surface effects are changing the order of reactivity, some conclusions may be drawn.[24]

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(23) L. DeHaes and G. Smets, *Bull. soc. chim. Belg.*, **59**, 13 (1950).

(24) Expressing r_1 in terms of the activation energies and the steric factors, one obtains the expression

$$r_1 = \frac{k_{11}}{k_{12}} = \frac{P_{11}Z_{11}}{P_{12}Z_{12}}\, e\, \frac{-\Delta H_{11} - \Delta H_{12}}{RT}$$

Using the above values for the system α-methylstyrene–*p*-chlorostyrene in this equation, one obtains the following pair of equations, corresponding to the temperatures 0° (273° absolute) and −78° (195° absolute)

$$\ln 15.5 = \ln \frac{P_{11}Z_{11}}{P_{12}Z_{12}} - \frac{\Delta H_{11} - \Delta H_{12}}{2 \times 273}$$

$$\ln 28 = \ln \frac{P_{11}Z_{11}}{P_{12}Z_{12}} - \frac{\Delta H_{11} - \Delta H_{12}}{2 \times 195}$$

Solution of these simultaneous equations leads to a value for the ratio $P_{11}Z_{11}/P_{12}Z_{12}$ of 3.5. The difference in the energies of activation, $\Delta H_{12} - \Delta H_{11}$, is approximately 0.8 kcal. Thus, the steric effect is very small, whereas, considering the low activation energies required for propagation, the energy factor is appreciable. The difficulties inherent in determining temperature effects in copolymerization reactions have been pointed out by Mayo and Walling[3]: ". . . . Measurements of temperature coefficients require extreme care. If the monomer reactivity ratios are close to unity, they can be measured accurately, but the change with temperature is small; if they differ greatly from one, they cannot be determined with precision."