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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, POLYTECHNIC INSTITUTE OF BROOKLYN]

Ionic Polymerization. IX. The Effect of Water in the Cationic Polymerization of Styrene Catalyzed by Stannic Chloride¹

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This work was undertaken in order to obtain information on the mechanistic role of water on the polymerization of styrene catalyzed by stannic chloride. The polymerization and molecular weight were studied as a function of the concentration of water and of the other reagents in a nitrobenzene-carbon tetrachloride solvent medium at 25°. Unusually stringent drying conditions and a quantitative measure of water permitted the water content in these experiments to be known with high accuracy and allowed data to be obtained not available from previous work. A high vacuum technique was employed for introduction of all reagents, and the polymerization rate was following dilatometrically. The initial rate of the reaction was observed to increase to a maximum and then decrease as the initial concentration of water was increased. The decrease in rate has been attributed partly to heterogeneity. At a constant initial water concentration, the reaction was found to be first order with respect to the stannic chloride concentration between 0.005 and 0.02 *M*, and approximately second order with respect to the monomer concentration between 1 and 3 *M*. The degree of polymerization of the resulting polymer increases with the initial monomer concentration, decreases with the water concentration, and is essentially independent of the catalyst concentration. A reaction mechanism has been proposed to account for these results, in which a monohydrate catalyst-cocatalyst complex is assumed. Termination is postulated to occur by a spontaneous unimolecular process and a bimolecular process involving water. A monomer transfer step is also indicated.

Although it is now generally believed that a cocatalyst is essential in the polymerization of olefins catalyzed by metal halides, very little information is available on the quantitative effects of cocatalysts in cationic polymerization.³

A qualitative investigation of the effect of trichloroacetic acid as a cocatalyst on the reaction rate of styrene catalyzed by titanium tetrachloride in hexane and toluene solvents was made by Plesch.⁴ The effect of water on the reaction rate for the same monomer and catalyst system in ethylene dichloride solvent also was studied. No molecular weight data were presented in these studies. In particular in only two previous cases has the quantitative effect of water on the rate and molecular weight in cationic polymerization been reported.^{5,6} The former work was con-

cerned with the polymerization of isobutene at -78.5° catalyzed by stannic chloride in the presence of ethyl chloride as solvent. Only semi-quantitative molecular weight data were reported. In the latter case,⁶ α -methylstyrene was polymerized to low molecular weight polymers (dimers, trimers, etc.) by stannic chloride catalyst in ethyl chloride solvent. Polymerization to obtain high molecular weight material was not studied. The reaction was conducted primarily at 55° at a catalyst-cocatalyst ratio of 1 to 3. Thus, this present work was undertaken in order to obtain knowledge of the polymerization reaction with respect to water as the cocatalyst in the polymerization of styrene to high polymer and to ascertain the mechanistic role of water in the polymerization.

The system chosen for study was the polymerization of styrene catalyzed by stannic chloride in a mixed solvent medium of nitrobenzene-carbon tetrachloride at 25°, since previous work in this Laboratory had provided considerable knowledge about the system. The rate of polymerization was followed dilatometrically, and a high vacuum technique was employed for introduction of the reagents into the dilatometer. Stringent drying of the reagents was employed. In a 30/70% mixture of nitrobenzene-carbon tetrachloride, the dependence

(1) This is the ninth in a series of papers concerned with ionic polymerization. For the eighth paper, see C. G. Overberger, B. M. Pearce and D. Tanner, *THIS JOURNAL*, 80, 1761 (1958).

(2) From the dissertation submitted by R. J. Ehrig to the Graduate School of the Polytechnic Institute of Brooklyn in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(3) For the most recent review of cationic polymerization see D. C. Pepper, *Quart. Revs.*, 8, 88 (1954).

(4) P. H. Plesch, *J. Chem. Soc.*, 1653, 1659, 1662 (1953).

(5) R. G. W. Norrish and K. E. Russell, *Trans. Faraday Soc.*, 48, 91 (1952).

(6) F. S. Dainton and R. H. Tomlinson, *J. Chem. Soc.*, 151 (1953).

of the initial rate on the initial water concentration was first determined. The kinetic order of the reaction with respect to catalyst and monomer at a constant water concentration was then ascertained. Finally, the dependence of the degree of polymerization of the resulting polymer on the catalyst, co-catalyst and monomer concentrations was determined. A preliminary investigation of the effect of water on the rate and molecular weight in a 15/85% mixture of nitrobenzene-carbon tetrachloride also has been made.

Experimental

Materials.—Carbon tetrachloride, C.P. (Fisher Certified), was dried successively over calcium chloride and phosphorus pentoxide and distilled from phosphorus pentoxide through a 12-inch Vigreux column, a constant boiling middle cut being retained. This was stored in a brown glass bottle over phosphorus pentoxide sealed with paraffin wax. A portion of this material was redistilled in the same manner as above, the middle cut being distilled into a vessel containing fresh anhydrous phosphorus pentoxide, b.p. 76.5° (atm.), n_D^{25} 1.4570 (n_D^{20} 1.4574*). After vigorous shaking of the vessel, it was attached directly to a high vacuum system and served as the storage vessel.

Nitrobenzene, C.P. (Fisher Certified), was washed with 1:1 sulfuric acid, water, 10% aqueous sodium hydroxide (until the aqueous layer was colorless) and finally with water (until alkali free). It was then dried over anhydrous calcium sulfate and alumina and fractionally distilled under reduced pressure, a middle 60% cut being retained. This was stored in a brown glass bottle over anhydrous silica gel sealed with paraffin wax and shaken occasionally. A portion of this material was fractionally redistilled in an atmosphere of dry nitrogen under reduced pressure from fresh phosphorus pentoxide into a vessel containing fresh anhydrous phosphorus pentoxide, a middle 60% cut being taken. The refractive index of the fore-run was n_D^{25} 1.5518 (n_D^{20} 1.5529*). After vigorous shaking of the vessel, it was attached directly to a high vacuum system and served as the storage vessel.

In later experiments the phosphorus pentoxide was replaced by anhydrous barium oxide for two reasons: (1) the nitrobenzene darkened upon standing, and (2) the necessity of heating the nitrobenzene *in vacuo* for efficient distillation raised the possibility of contamination by more volatile compounds. Changing drying agents had no apparent effect on the reaction rates.

Commercial styrene (Dow Chemical Co.) was washed free of inhibitor with 5% aqueous sodium hydroxide, washed until neutral with distilled water and then dried over anhydrous magnesium sulfate. It was then distilled under reduced pressure from anhydrous silica gel through a 12-inch Vigreux column and stored in a brown glass bottle sealed with paraffin wax in a refrigerator. A fraction of this material was stored in a refrigerator overnight over fresh anhydrous barium oxide. The redried styrene was then redistilled in an atmosphere of dry nitrogen from barium oxide under reduced pressure into a vessel containing fresh, crushed anhydrous barium oxide and a small quantity of trinitrobenzene, a middle fraction being taken. The refractive index of the fore-run was n_D^{25} 1.5438 (n_D^{20} 1.5441*). After the vessel had been shaken vigorously, it was attached directly onto a high vacuum system and served as the storage vessel.

Anhydrous stannic chloride, C.P. (Fisher Certified), was refluxed overnight over anhydrous phosphorus pentoxide in an all-glass apparatus protected by a tube filled with phosphorus pentoxide. The drying tube was then removed and replaced by a short Vigreux column connected to a fraction cutter and a receiving vessel containing fresh, anhydrous phosphorus pentoxide. The entire apparatus was then flame-dried for ten minutes at a slightly reduced pressure. After cooling the apparatus, the stannic chloride was dis-

tilled into the vessel under reduced pressure. The receiving vessel was constructed with two stopcocks and two ground glass joints in order that it could be removed from the distillation apparatus and attached to a high vacuum system without exposure to the atmosphere.

Doubly distilled water was redistilled in an all-glass apparatus. The receiving vessel was attached directly to a high vacuum system and served as the water storage vessel.

Methyl ethyl ketone (b.p. 79.5° (atm.)) and methyl alcohol (b.p. 64.5° (atm.)) were employed in the purification of the polymers.

All drying agents were of the highest purity available and were used without further purification. The materials were never exposed to the atmosphere for prolonged lengths of time and were discarded at the first signs of deliquescence.

The catalyst, monomer and solvents were further treated in an all-glass high vacuum apparatus designed specifically to minimize adventitious moisture and to permit quantitative measurements of water.¹⁰

Polymerization Technique.—Vacuum-sealed dilatometers, thermostated at 25°, were employed for studying the reaction rate. The polymerization was followed to approximately 10% conversion. The polymers from the dilatometers were precipitated in methanol, filtered, reprecipitated from methyl ethyl ketone, washed and dried. Conversions were calculated from the isolated polymer weights, and the initial weight fraction of monomer. The results were in approximate agreement with the percentage conversion calculated from the dilatometric studies if the time intervals and the polymer remaining in the dilatometers were taken into consideration. These polymers, so treated, were used in subsequent molecular weight determinations and infrared studies.

The intrinsic viscosity determinations and molecular weight calculations were made in the same manner as described previously.¹¹

Treatment of Experimental Data.—The experiments conducted in 15% nitrobenzene, 85% carbon tetrachloride were frequently irreproducible. At high concentrations of water (0.015, 0.02 and 0.03 *M*) the system was heterogeneous and never reproducible. With water concentrations of 0.010 and 0.012 *M*, the rates were reproducible, but the molecular weights were not. This was attributed to incipient heterogeneity and the results are not included herein for the reasons mentioned.

For the results of the experiments included herein, the data were treated in the following manner. Based on the assumption that the contraction in volume is directly related to the percentage polymerization, the change in height of the dilatometers was calculated to percentage polymerization by the use of the conversion factors given in Table I.

TABLE I
DILATOMETER CONVERSION FACTORS*

Styrene, moles/l.	Dilatometer I	Dilatometer II
1.00	...	0.702
1.21	...	.580
1.48	...	.475
2.00	0.327	.351
2.50	.260	...
3.01	.216	...

* Used in converting contraction in volume to percentage polymerization by multiplying the change in height in centimeters by the conversion factor.

These conversion factors were obtained using the density of the monomer (0.907 g./ml. at 20°¹²) and the effective density of polystyrene in solution of a good solvent (1.07 g./

(7) C. G. Douglas, *J. Phys. Chem.*, **49**, 358 (1945).

(8) "International Critical Tables," Vol. I, McGraw-Hill Book Co., Inc., New York, N. Y., 1926, p. 278.

(9) E. R. Blout and H. Mark, "Monomers," Interscience Publishers, Inc., New York, N. Y., 1951, p. 47.

(10) Experimental details of purification and the polymerization technique employed are available from the doctoral dissertation of Raymond J. Ehrig, titled "The Effect of Water in the Cationic Polymerization of Styrene by Stannic Chloride. A Kinetic Study," Publication No. 21, 415, University Microfilms, 313 No. First Street, Ann Arbor, Mich.

(11) G. F. Endres and C. G. Overberger, *THIS JOURNAL*, **77**, 2201 (1955).

(12) G. Egloff, "Physical Constants of Hydrocarbons," Vol. III, Reinhold Publishing Corp., New York, N. Y., 1946, p. 188.

ml.¹³). The theoretical change in volume calculated from the above densities is 0.168 cc./g. Pepper¹⁴ showed good agreement between calculated and observed values of the change in height corresponding to complete polymerization when a bulk shrinkage factor of 0.170 cc./g. was employed. This was done at a temperature of 25° in a solution of ethylene dichloride at a styrene concentration of 181 g./l. Okamura and Higashimura¹⁵ obtained a bulk shrinkage factor of 0.172 cc./g. from density measurements in ethylene dichloride at a temperature of 30°. A bulk shrinkage factor of 0.152 cc./g. was determined in these laboratories¹⁶ from density measurements at 0° in a solution of 50% nitrobenzene, 50% carbon tetrachloride. It was considered reasonable to use the above mentioned density values 152–172 for correlating the dilatometric height changes to percentage polymerization since the percentage of polymer isolated was in good agreement with the dilatometric polymerization, provided the necessary time intervals from the beginning to the cessation of the reaction were included. Also, estimates of the shrinkage factor based on comparison of the extent of meniscus fall for the very slow reactions with the percentage conversions of the isolated polymer differed only by a maximum of 4% from the factor employed. The difference is actually less since the amount of unrecoverable polymer left in the dilatometer was not taken into consideration. Since errors of this magnitude are within the estimated experimental error, 0.168 cc./g. was considered as representing the true shrinkage factor.

The converted data were represented graphically as percentage polymerization *versus* time (zero time was considered as the initial reading of the dilatometer). For the experiments conducted in 30% nitrobenzene, 70% carbon tetrachloride, the reaction rates were obtained directly from the curves by measuring the slopes at the initial curvature and at 7% conversion multiplied by the initial concentration of monomer. The former slopes were obtained using the two point slope formula and the latter by the mirror technique. The rates were calculated at 7% conversion for all experiments conducted in 30% nitrobenzene with the exception of those conducted at high monomer concentrations, since it was impossible to obtain a rate beyond the extent of the dilatometer. These 7% rates were easier to estimate than the rates calculated for the initial reaction since the conversion-time curves exhibited a closer proximity to linearity as the polymerization continued. The calculation of the slope at this conversion, therefore, is less subject to error and is not affected by any extraneous initial effects. However, the strong curvatures exhibited by the initial reaction are not attributed to temperature effects, since similar systems¹⁷ not employing dilatometers also exhibit the same general shape.

The order of the reaction with respect to monomer and catalyst was obtained from a log-log plot of reaction rate *versus* concentration.

The rates for the experiments conducted in 15% nitrobenzene, 85% carbon tetrachloride have been obtained from the maximum slope since the reaction exhibited an induction period and the conversion-time curves exhibited strong curvatures throughout the reaction.

Results

Variation of the Water Concentration.—In Fig. 1 is given a composite diagram of the conversion-time curves obtained for the polymerization in a mixture of 30% nitrobenzene, 70% carbon tetrachloride when the water concentration is varied. Similar curves were obtained for variations of the monomer and catalyst concentration. No induction periods were observed even at the lowest concentrations of water, and, if an induction period exists, it is less than ten minutes in duration. The reaction is fast followed by a quick deceleration in

rate which is evident from the curves in Fig. 1. In Table II are listed the changes in rate and degree of polymerization which occurred with varying concentrations of water. Results for the rate have been given for the initial reaction and when it is 7% completed. Both calculations have been made throughout this study to indicate the change in rate that is occurring during polymerization. The rate of polymerization was reduced to approximately 5% of the maximum rate by mixing the "dry" reagents and the rate increased by successive additions of water, the maximum in rate occurring at approximately a 1:1 ratio of water to stannic chloride.

TABLE II

EFFECT OF WATER ON THE POLYMERIZATION OF STYRENE IN NITROBENZENE (30%)–CARBON TETRACHLORIDE (70%) SOLUTION

(Styrene) = $2.00 \pm 0.01 M$; (stannic chloride) = $0.020 \pm 0.001 M$; temp. = $25.00 \pm 0.01^\circ$

(H ₂ O) × 10 ³ moles l. ⁻¹	Init. rate ^a × 10 ⁴ moles l. ⁻¹ min. ⁻¹	Rate at 7% conv. ^b × 10 ⁴ moles l. ⁻¹ min. ⁻¹	Conv. (%) of iso- lated polymer	$[\eta]$ 50 cc. g. ⁻¹	$\bar{P}_n$
"None"	2.53	3.68	6.9	0.217	116
"None"	2.63	2.78	7.1	.214	114
0.8	9.29	8.05	8.9	.211	112
1.1	10.3	7.39	8.4	.209	111
1.9	17.8	12.4	8.1	.202	104
5.3	25.7	18.4	10.1	.201	104
5.4	23.7	18.7	9.6	.196	100
7.4	28.3	20.1	10.8	.202	104
9.8	26.5	21.4	11.8	.197	101
9.9	25.9	22.3	11.3	.195	100
14.9	47.6	28.7	13.2	.185	92
19.8	53.1	35.2	14.1	.171	81
28.5	45.6	29.1	11.0 ^c	.140	60

^a Rate obtained from tangents to conversion-time curve within 2% conversion. ^b Rate obtained from tangents to conversion-time curve at 7% conversion. ^c Part of sample lost during experiment.

Beyond an equimolar portion, the rate decreased which may be attributed to a low solubility of the active complex. The increase in rate was accompanied by a decrease in the degree of polymerization as is shown in Fig. 2, curve a, and it can be seen that the degree of polymerization decreases rapidly at higher water concentrations.

Variation of the Catalyst Concentration.—At a constant initial water concentration of 0.005 *M*, the stannic chloride concentration was varied over a fourfold range. The order of the reaction with respect to stannic chloride was 0.9 and 1.1 for the initial rate and the rate at 7% conversion, respectively. Table III lists the rates obtained together with the data for the degree of polymerization. The molecular weight of the polymer is essentially independent of the stannic chloride concentration (Fig. 3), although there is a decrease at the very low concentrations of stannic chloride. In many previous cases, the degree of polymerization has been found to be essentially independent of the catalyst concentration for cationic polymerization.³

Variation of the Monomer Concentration.—The initial monomer concentration was varied over a

(13) D. J. Streeter and R. F. Boyer, *Ind. Eng. Chem.*, **43**, 179 (1951).

(14) D. C. Pepper, *Trans. Faraday Soc.*, **45**, 404 (1949).

(15) S. Okamura and T. Higashimura, *J. Polymer Sci.*, **21**, 289 (1956).

(16) B. Fingerhut, private communication.

(17) J. George, H. Wechsler and H. Mark, *THIS JOURNAL*, **72**, 3891 (1950).

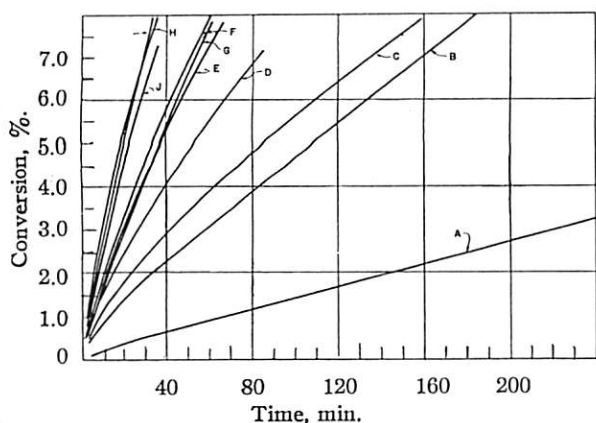


Fig. 1.—Polymerization in nitrobenzene (30%)–carbon tetrachloride (70%) solution at 25°; (styrene), $2.00 \pm 0.01M$; (SnCl_4), $0.020 \pm 0.001M$: A, no H_2O ; B, $0.8 \times 10^{-3}M$ H_2O ; C, $1.1 \times 10^{-3}M$ H_2O ; D, $1.9 \times 10^{-3}M$ H_2O ; E, $5.4 \times 10^{-3}M$ H_2O ; F, $7.4 \times 10^{-3}M$ H_2O ; G, $9.9 \times 10^{-3}M$ H_2O ; H, $14.9 \times 10^{-3}M$ H_2O ; I, $19.8 \times 10^{-3}M$ H_2O ; J, $28.5 \times 10^{-3}M$ H_2O .

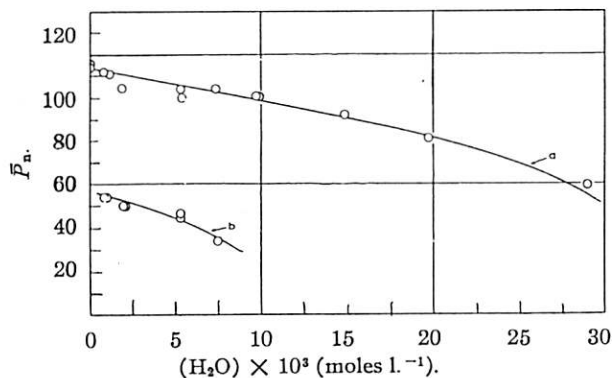


Fig. 2.—The effect of water on the degree of polymerization of styrene: a, nitrobenzene (30%)–carbon tetrachloride (70%); b, nitrobenzene (15%)–carbon tetrachloride (85%).

three-fold range (Table IV) at a constant initial water concentration of $0.005M$. The order of the reaction with respect to the initial monomer concentration was 2.5 and 2.0 for the initial rate and the rate at 7% conversion, respectively. Due to the uncertainty of the very initial part of the reaction, the rate of polymerization is considered to be second order with respect to monomer between 1.0 and 3.0 M styrene.

TABLE III

EFFECT OF STANNIC CHLORIDE ON THE POLYMERIZATION OF STYRENE IN NITROBENZENE (30%)–CARBON TETRACHLORIDE (70%)

(Styrene) = $2.00 \pm 0.01M$; (water) = $0.0053 \pm 0.0001M$; temp. = $25.00 \pm 0.01^\circ$

(SnCl_4) ^a $\times 10^3$ moles l. ⁻¹	Init. rate ^b $\times 10^4$ moles l. ⁻¹ min. ⁻¹	Rate at 7% conv. ^c $\times 10^4$ moles l. ⁻¹ min. ⁻¹	Conv. (%) of iso- lated polymer	$[\eta]$ 50 cc. g. ⁻¹	$\bar{P}_n$
5.0	8.32	3.83	7.9	0.166	78
7.0	9.21	6.36	7.0	.178	86
10.0	8.04	7.18	8.8	.191	96
10.0	12.1	7.90	7.6	.192	97
14.0	22.9	13.8	9.1	.194	99

^a For data at 20.0×10^{-3} mole l.⁻¹ SnCl_4 , see Table II. ^b See footnote a, Table II. ^c See footnote b, Table II.

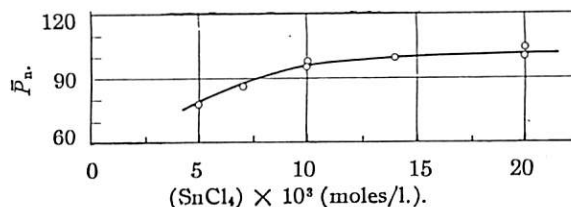


Fig. 3.—Effect of stannic chloride on the degree of polymerization of styrene.

The dependence of the degree of polymerization on the initial monomer concentration (Fig. 4) is seen to have a definite curvature and increases as the monomer concentration is increased. This type of relationship has been observed for other cationic polymerizations and has been explained by Endres and Overberger¹¹ on the assumption that there are two termination or transfer steps operating simultaneously, one unimolecular and the other involving monomer.

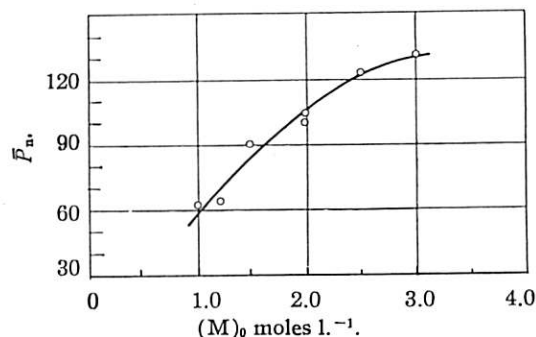


Fig. 4.—Effect of monomer concentration on the degree of polymerization of styrene.

Variation of the Water Concentration in the 15% Nitrobenzene–85% Carbon Tetrachloride System.

A preliminary study of the effect of water on the rate and the degree of polymerization in a solution of 15% nitrobenzene–85% carbon tetrachloride also was made and the graphical representation of the conversion–time course of the polymerization is given in Fig. 5. As can be seen from the curves, the reaction exhibited an induction period and it appeared that the time of induction increased with increasing concentrations of water, except perhaps at very low water concentrations. However, no

TABLE IV

EFFECT OF MONOMER ON THE POLYMERIZATION OF STYRENE IN NITROBENZENE (30%)–CARBON TETRACHLORIDE (70%)
(Stannic chloride) = $0.020M$; (water) = $0.053 \pm 0.0001M$; temp. = $25.00 \pm 0.006^\circ$

(M_0) ^a moles l. ⁻¹	Init. rate ^b $\times 10^4$ moles l. ⁻¹ min. ⁻¹	Rate at 7% conv. ^c $\times 10^4$ moles l. ⁻¹ min. ⁻¹	Conv. (%) of iso- lated polymer	$[\eta]$ 50 cc. g. ⁻¹	$\bar{P}_n$
1.00	4.94	4.17	16.5	0.143	62
1.21	6.10	5.80	13.1	.146	64
1.48	12.0	9.56	12.9	.183	90
2.50	43.8	31.3 ^d	9.1	.224	123
3.01	68.3	39.8 ^e	11.9	.234	131

^a For data at 2.0 moles l.⁻¹ styrene, see Table II. ^b See footnote a, Table II. ^c See footnote b, Table II. ^d Rate obtained from tangent to conversion–time curve at 6% conversion. ^e Rate obtained from tangent to conversion–time curve at 5% conversion.

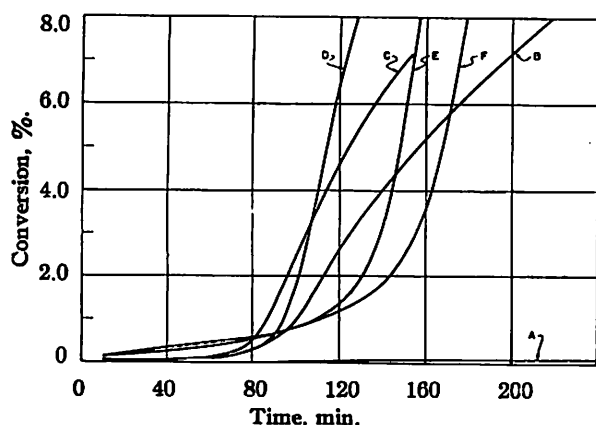


Fig. 5.—Polymerization in nitrobenzene (15%)–carbon tetrachloride (85%) solution at 25°; (styrene), $2.00 \pm 0.01M$; (SnCl_4), $0.020 \pm 0.001M$: A, no H_2O ; B, $0.8 \times 10^{-3}M \text{H}_2\text{O}$; C, $1.0 \times 10^{-3}M \text{H}_2\text{O}$; D, $2.0 \times 10^{-3}M \text{H}_2\text{O}$; E, $5.3 \times 10^{-3}M \text{H}_2\text{O}$; F, $7.5 \times 10^{-3}M \text{H}_2\text{O}$.

definite correlation of the induction period with water concentration could be made due to the variable times which elapsed before initial readings were taken. Induction periods have been observed previously in other styrene polymerizations catalyzed by stannic chloride^{15,18–20} and seem to be characteristic of reactions conducted in solutions of low dielectric constants. An increase in the induction period with increasing concentration of water has been indicated in two previous cases.^{15,18} The nature of the induction period has been attributed either to the presence of an impurity²¹ or to an inhibition of the reaction caused by traces of HCl which may be formed by hydrolysis of the catalyst.^{18,20}

The changes in rate and degree of polymerization which occurred with varying concentrations of water are listed in Table V. The results for the rate of the reaction are given as the maximum rate occurring between 0–10% conversion. A mixture of the "dry" reagents gave a negligible rate and was approximately one hundredth as fast as the rate of the reaction with the smallest quantity of water added. As the quantity of water was increased, the rate rose sharply to a maximum approximately at a 4:1 ratio of stannic chloride to water and then decreased. Further experiments conducted at higher water concentrations were marked by the appearance of a very slight opalescence in the reaction mixture, but the rates were in the same order of magnitude as that of the 0.0075 M water. The fall off in rate, therefore, is probably due to a heterogeneous reaction.

A comparison of the data in Tables II and V shows that the polymerization rate is smaller by a factor of two in 30% nitrobenzene–70% carbon tetrachloride than it is in 15% nitrobenzene–85% carbon tetrachloride, at the same concentrations of the reactants. The fact that the rate is not considerably larger in the more polar solution sug-

gests that there is a selective solvation of the reacting ions by the nitrobenzene. Evidence for selective solvation in other systems has been presented by Amis and co-workers.²²

TABLE V
EFFECT OF WATER ON THE POLYMERIZATION OF STYRENE IN NITROBENZENE (15%)–CARBON TETRACHLORIDE (85%) SOLUTION

(Styrene) = $2.00 \pm 0.01 M$; (stannic chloride) = $0.0205 \pm 0.0005 M$; temp. = $25.00 \pm 0.008^\circ$

$(\text{H}_2\text{O}) \times 10^3$ moles l. ⁻¹	Maximum rate $\times 10^4$ moles l. ⁻¹ min. ⁻¹	Conv. (%) of isolated polymer	$[\eta]$ 50 cc. g. ⁻¹	$\bar{P}_n$
"None"	0.136 ^a	0.4	...	..
"None"	0.058 ^a	0.3	...	..
"None"	0.191 ^a	0.6	...	..
0.8	16.3	7.0	0.131	54
1.0	21.7	6.1	.131	54
1.0	23.3	6.7	.131	54
1.9	37.2	8.0	.123	50
2.0	42.7	8.7	.123	50
5.3	60.3	9.2	.116	45
5.3	63.3	10.7	.119	47
7.5	56.4	8.9	.095	34

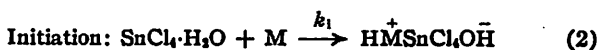
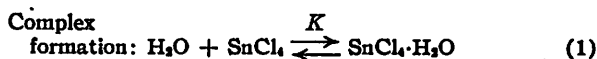
^a Rate obtained from tangents to conversion–time curve at 0.4% conversion.

The effect of variation of the water on the degree of polymerization of the polymers isolated from the reaction rate measurements is given in Fig. 2 (curve b). It can be seen that there is a decrease in the molecular weight as the water concentration is increased with a greater change occurring at higher water concentrations.

The data for the extent of polymerization of each experiment have been included in the latter four tables, and it can be seen that the percentage conversion of the isolated polymer varied according to how fast the reaction was occurring. Since the intrinsic viscosities were determined on these polymers, there is the possibility that the observed changes of the degree of polymerization may be due to the conversion differences. However, it has been shown for similar systems that the degree of polymerization is independent of the conversion from 20 to 80%,²³ and from 11 to 90%.²⁴ Okamura and Higashimura¹⁵ reported that the molecular weights of the polystyrenes did not decrease during polymerization in benzene or carbon tetrachloride solutions.

Discussion

Although an exact interpretation of the reaction cannot be made from the above kinetic results, a possible reaction mechanism which accounts for these observations may be formulated in the manner



(22) E. S. Amis, *J. Chem. Phys.*, **26**, 880 (1957), and references cited therein.

(23) G. F. Endres, Dissertation for the Degree of Doctor of Philosophy, Polytechnic Institute of Brooklyn, 1954, p. 30.

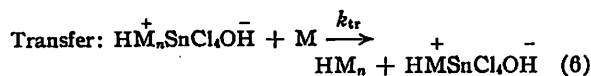
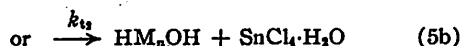
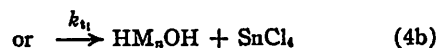
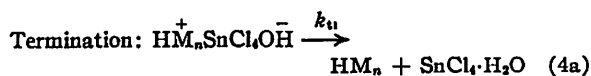
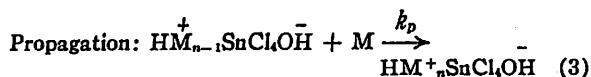
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Assuming a steady state with respect to active centers (HM_n^+), and using the equilibrium relation⁷

$$(\text{SnCl}_4 \cdot \text{H}_2\text{O}) = K(\text{SnCl}_4)(\text{H}_2\text{O}) \quad (7)$$

it can be shown that the rate of disappearance of monomer and the degree of polymerization, $\bar{P}_n$, are given in eqs. 8 and 9

$$-d(\text{M})/dt = (Kk_p k_p (\text{SnCl}_4)(\text{H}_2\text{O})(\text{M})^2)/k_{t1} + k_{t2}(\text{H}_2\text{O}) \quad (8)$$

$$\bar{P}_n = k_p(\text{M})/(k_{t1} + k_{t2}(\text{H}_2\text{O}) + k_{tr}(\text{M})) \quad (9)$$

In equations 8 and 9, (H_2O) and (SnCl_4) denote the concentrations of free water and stannic chloride. They are essentially equal to the corresponding stoichiometric concentrations when these reagents are largely free rather than bound as $\text{SnCl}_4 \cdot \text{H}_2\text{O}$. To explain the data on the basis of the mechanism given by equations 1 to 6 it will be necessary to assume that these reagents are largely free.

The above rate expression 8 adequately describes the first- and second-order dependence of the rate on the catalyst and monomer concentrations, respectively, assuming that the catalyst is largely free. This order has been found generally for many open dilatometric systems for styrene and vinyl ethers.³ In the polymerization of α -methylstyrene,⁶ however, Dainton found the order of the reaction with respect to the catalyst concentration to be 1.42 at 25° at a cocatalyst-catalyst ratio exceeding 3. Variation of the monomer concentration indicated an order of unity at low concentrations, and rising above this value as the monomer concentration was increased, the average value of the order was 1.4 between 0.32 and 0.80 *M*. For the system isobutene-stannic chloride-ethyl chloride, Norrish and Russell⁵ found a continual increase in rate with increasing stannic chloride concentrations. At equimolar proportions of stannic chloride and water (0.19 mole %) the rate became approximately independent of the catalyst concentration. A further investigation of this system²⁵ indicated a first-order dependence of the rate with respect to the monomer concentration between 4 and 20 mole per cent.

The results obtained in this work (Table II) indicated that the rate of the reaction increases to a maximum value and then decreases. On the other hand, according to equation 8 the reaction rate should increase with increasing water con-

centration and should approach a maximum value and finally should become independent of the water concentration. The maximum occurs at a ratio of about 1:1 water to stannic chloride in the case of the 70-30 solvent mixture and at a ratio of 1:4 water to stannic chloride in the case of the 85-15 solvent mixture. This apparent contradiction of the proposed mechanism with the results obtained may be explained on the possibility that beyond a certain mixture of water and stannic chloride, a dihydrate may be formed which is insoluble in the reaction medium, is unable to initiate chains, and causes a decrease in the reaction rate by nature of a two phase system being formed. For the polymerization of α -methylstyrene⁶ Dainton also found that the rate of polymerization increased with increasing water concentration and reached a maximum rate at approximately a 1:1 ratio of stannic chloride to water. When the ratio of added water to a catalyst concentration exceeded 3:1, the initial rate of polymerization became independent of the amount of water present, a somewhat different behavior than the case reported here. In the isobutene case,⁵ however, the rate was proportional to the amount of added water up to 0.3 mole % (stannic chloride = 1.15 mole %), but the proportionality decreased beyond this concentration. The α -methylstyrene case more closely approximates our results for the 30-70 solvent mixture.

The observed decrease of the degree of polymerization with increasing concentrations of water may be explained on the basis of a new concept, a termination process involving free water (5a or b). The probability that there is free water in the reaction medium may be assumed on the basis of the results obtained since it has been shown that at a water-stannic chloride ratio of 1:4 the reaction is dependent upon the first power of the stannic chloride which indicates that even in an excess of stannic chloride the equilibrium expressed in equation 1 is still displaced to the left leaving a large percentage of water free and available for termination.

As noted previously in this work, the molecular weight of the polymer is essentially independent of the stannic chloride concentration with a small decrease at very low concentrations of stannic chloride.

Norrish and Russell⁵ found the molecular weight of polyisobutene to be inversely proportional to the amount of water added as noted here and directly proportional to the monomer concentration, a relationship not found in this work. At a constant water concentration, they found that the molecular weight had a minimum value at equimolar proportions of stannic chloride and water and then increased with increasing stannic chloride concentrations. Dainton⁶ found the degree of polymerization of poly- α -methylstyrene increased with increasing monomer concentrations but was independent of the catalyst cocatalyst concentration.

The mechanistic scheme presented here shows two possible means of termination for both the unimolecular and the bimolecular process. No definite postulation as to which of the two is occurring can be envisioned at this time. On the other hand

the behavior of the % conversion-time plots at low water concentrations suggests that the water concentration may be decreasing as the reaction proceeds. Infrared spectra of the polymers isolated from the experiments conducted at various concentrations of water, stannic chloride and monomer showed no definite bands for hydroxyl groups. If termination is occurring by process 4a or 5a, the polymers should possess a terminal olefin, but infrared spectral data exhibited no bands characteristic of a double bond. The lack of terminal unsaturation in poly- α -methylstyrenes prepared by stannic chloride in ethyl chloride solution has been attributed by Dainton⁶ to an intramolecular rearrangement forming a cyclic structure. It is possible that polystyrenes prepared in a similar manner may achieve saturation by the same sequence.

In order to evaluate the results obtained with relation to the rate equation, it was found advantageous to estimate the amount of adventitious water present throughout the investigation. An approximation of the water present beyond the measured quantity was made by extrapolating the rate *versus* water concentration curve to zero rate. A number of such extrapolations were made from various sections of the curves and an average value of approximately 3.0×10^{-4} g. (~ 0.001 M) of water was calculated. This value has been added to the measured concentrations of water and the experimental curves obtained for the initial rate (curve b) and the rate at 7% conversion (curve c) as a function of the corrected water concentration for the system 30% nitrobenzene, 70% carbon tetrachloride are given in Fig. 6.

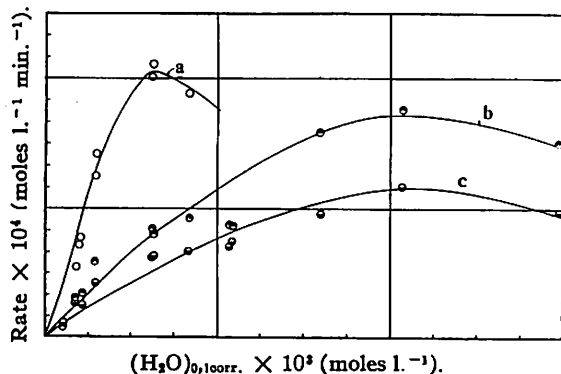


Fig. 6.—The effect of water on the initial rate (b, $\bullet$), the rate at 7% conversion (c, $\circ$) in nitrobenzene (30%)–carbon tetrachloride (70%) solution and on the maximum rate (a, $\circ$) in nitrobenzene (15%)–carbon tetrachloride (85%) solution.

From the above mechanism and subsequent equations, a number of ratios of rate constants can be derived from the data obtained for the solvent system, 30% nitrobenzene–70% carbon tetrachloride. At a constant water concentration, an intercept of $k_{tr}/k_p = 2.5 \times 10^{-3}$ and a slope of $(k_{ti} + k_{ti}(H_2O))/k_p = 1.5 \times 10^{-2}$ mole l.⁻¹ is obtained. In a similar manner, from a plot of the reciprocal degree of polymerization against the initial corrected water concentration, the values k_{ti}/k_p (M) = 16×10^{-2} l. mole⁻¹ and k_{ti}/k_p (M) + $k_{tr}/k_p = 8.6 \times 10^{-3}$ are obtained from the slope and intercept, respectively. In obtaining the latter two values, the one point derived

from the data where the rate is decreasing has not been considered since it is obvious that beyond an equimolar ratio of water and stannic chloride the rate and degree of polymerization are no longer governed by the equations derived. From the four values obtained above, the following individual ratios of rate constants can be derived: $k_{tr}/k_p = 2.5 \times 10^{-3}$; $k_{ti}/k_p = 1.2 \times 10^{-2}$ mole l.⁻¹; $k_{ti}/k_p = 3.2 \times 10^{-1}$. The value obtained here for k_{tr}/k_p which is the ratio of the velocity constants for monomer transfer over propagation is the same as has been reported by Endres and Overberger¹⁷ for the polymerization of styrene by stannic chloride in a mixture of nitrobenzene and carbon tetrachloride at 0° in a bottle system. The ratio k_{ti}/k_p , however, differs approximately by a factor of two between the value presented here and that of Endres and Overberger¹¹ and this difference may be attributed to a temperature variation. In reference to the same work by Overberger, the ratio k_{ti}/k_p obtained in this present study may be considered to be the molecular termination constant for water and the value obtained is found to be less than that reported for thiophene by a factor of three. It is noteworthy here that Endres²⁸ found that the degree of polymerization decreases with increasing conversion for compounds with molecular termination constants less than one. However, it was also observed that the average degree of polymerization was sensitive to changes in conversion when the molecular termination constant differed from one by a factor of 10², but was insensitive to minor changes with conversion when the difference was of the order of two. The molecular termination constant obtained for water in this present study differs from one by a factor of three, and, therefore, the degree of polymerization should be only slightly affected by conversion. Although water, either free or bound in some form, has been observed to decrease the degree of polymerization in this investigation, it may not, however, be a true molecular terminating agent. The previously reported terminating agents were observed to have either retarded the rate of polymerization or have no effect whatsoever. In one case where the rate was accelerated, the increase was possibly due to an increase in the dielectric constant of the medium. In this present study, it has been shown that water accelerates the rate which could not possibly be due to an increase in the dielectric constant of the medium since it is present in such small amounts.

It can be seen from the constants derived above that another constant (k_{ti}/k_{ti}) may be obtained. This is the ratio of the rate constants for unimolecular termination to that of bimolecular termination and has a value of 3.8×10^{-2} mole l.⁻¹. This ratio may also be derived independently from the rate expression (equation 8). Upon taking reciprocals of the rate equation, the expression $1/\text{rate} = k_{ti}/Kk_i k_p (\text{SnCl}_4)(\text{H}_2\text{O})(\text{M})^2 + k_{ti}(\text{H}_2\text{O})/Kk_i k_p (\text{SnCl}_4)(\text{H}_2\text{O})(\text{M})^2$ is obtained and from the values of the slope and intercept obtained by a plot of $1/\text{rate}$ *versus* $(1/\text{H}_2\text{O})_{\text{corrected}}$, the ratio k_{ti}/k_{ti} may be derived. An average value of 1.5×10^{-2} mole l.⁻¹

(26) See ref. 23, p. 44.

is obtained from the initial rate and the rate at 7% conversion.

It is of interest to note that if the equations employed above are applicable to the data obtained from the system employing 15% nitrobenzene, 85% carbon tetrachloride, the values obtained for the ratio of k_t/k_i from the degree of polymerization and from the rate expression are in the same order of magnitude as that obtained from the system employing 30% nitrobenzene, 70% carbon tetrachloride. From the data for the 15% nitrobenzene case, the values obtained for k_t/k_i from the degree of polymerization and from the rate measurements are 2.1×10^{-2} mole l^{-1} and 2.5×10^{-2} mole l^{-1} , respectively. The ratio of k_{tr}/k_p obtained from the degree of polymerization data for the 30% nitrobenzene system has been employed in deriving k_t/k_i from the degree of polymerization data for the 15% nitrobenzene system. Since this ratio was the same value obtained by Endres and Overberger¹¹ for the system employing a nitrobenzene mixture (40% by volume) at a temperature of 0°, it is unlikely that the value would change in going from a 30 to a 15% mixture of nitrobenzene at 25°. The assumption of a constant value may therefore be made.

The corrected experimental curve for the effect of water on the maximum rate of polymerization for

the system employing 15% nitrobenzene, 85% carbon tetrachloride is given in Fig. 6, curve a.

The various ratios of rate constants derived above may also be calculated from the data obtained without employing the corrected water concentration mentioned above. If this is done, it is found that there is essentially no difference between the constants derived from the degree of polymerization data whether the corrected or uncorrected water concentrations are employed, since it can be seen from the results obtained that the degree of polymerization is little affected by small changes of the water concentration. However, a difference between the corrected and uncorrected values obtained for the constants derived from the rate data is found and this is understandable since it has been observed that the rate of polymerization varies considerably with small changes of the water concentration.

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