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in Copolymerization.

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Ionic Polymerisation¹. Ion Pair Chain Mechanisms. The
Effect of Different Lewis Acid Catalysts on the Monomer
Reactivity Ratios in Copolymerisation.

by G. G. Overberger, R. J. Ehrig² and David Tanner.

ABSTRACT

With the copolymer system styrene, p-chlorostyrene in solvent mixtures of carbon tetrachloride and nitrobenzene, no difference in monomer reactivity ratios were obtained with aluminum bromide, ferric chloride, titanium tetrachloride, stannic chloride and titanium tetrachloride-trichloroacetic acid as catalysts in homogeneous solution. In these solvent systems with the above catalysts no measurable fragments from the solvent or catalysts were incorporated in purified polystyrenes obtained from styrene alone with the exception of aluminum bromide in pure nitrobenzene as a solvent and antimony pentachloride in a 1:1 carbon tetrachloride nitrobenzene solution. The insensitivity of monomer reactivity ratios in this system to changes in dielectric constant and

catalyst concentration previously noted with a stannic chloride catalyst was verified with other catalysts.

In a previous paper, the effect of reaction conditions on the monomer reactivity ratios for the copolymerization of

- 1) This is the third in a series of papers concerned with ionic polymerization. For the second paper, see C. G. Overberger, L. H. Arond, D. Tanner, J. J. Taylor and T. Alfrey, Jr., THIS JOURNAL, 74, 4848 (1952). A portion of this work was supported by a contract from the Office of Naval Research.
- 2) A portion of a thesis submitted by R. J. Ehrig in partial fulfillment of the requirements for the degree of Master of Science to the graduate school of the Polytechnic Institute of Brooklyn.

styrene and p-chlorostyrene was investigated in order to use this technique to study the mechanism of ion pair addition to the double bond³. An important variable which was not included

- 3) C. G. Overberger, L. H. Arond, J. J. Taylor, THIS JOURNAL, 73, 5541 (1951)

ed in the previous work is the effect of variation in types of catalyst. Information of this type was sought in order to aid in the elucidation of the mechanism of the propagation step¹. In addition, it was desirable to determine whether any fragments from the catalysts or solvent remained in the polymer chain after purification. This paper reports the monomer reactivity ratios obtained for the system styrene-p-chlorostyrene in carbon tetrachloride, nitrobenzene mixtures titanium tetrachloride, or in pure nitrobenzene for ferric chloride, titanium tetra-

chloride-trichloroacetic acid and aluminum bromide. Additional data obtained with stannic chloride in pure nitrobenzene and with aluminum bromide in pure carbon tetrachloride are also reported. The anomalous behavior of antimony pentachloride is noted.

EXPERIMENTAL

Solvents and Monomers.

Carbon tetrachloride, nitrobenzene, styrene and p-chloro-styrene were purified as described previously³,

Catalysts.-

Stannic chloride was purified and ampules prepared according to the procedure described previously³.

Titanium tetrachloride, C.P., (Eimer and Amend) was purified in the same manner as the stannic chloride except that the titanium tetrachloride was refluxed with a small amount of very fine, pure copper strips to remove the last traces of light color⁴ in the titanium tetrachloride. The

4) C. K. Stoddard and E. Piets, U.S. Bur. Mines, Rept. Invest. 4153, 1947; see C.A. 42, 2406 (1948)

titanium tetrachloride was distilled under nitrogen and ampules were prepared in a nitrogen atmosphere as previously described³. The filled ampules were colorless.

Anhydrous ferric chloride, C.P., (Eimer and Amend) was purified by sublimation in an apparatus similar to that described for the preparation of the Lewis acid by B. R. Tarr⁵.

A few minor changes were necessary. After the apparatus was

5) B. R. Tarr, "Inorganic Syn.", Vol. III, McGraw-Hill Book Company, Inc., New York, 1950, p. 191.

flame dried, ferric chloride was quickly put into the reaction chamber. This entire apparatus was then swept with dry nitrogen and again flame dried. If any yellow coloration due to hydration was detected at this stage, the apparatus was dismantled, redried, and a new sample was prepared. Dry chlorine gas was then allowed to flow into the system by means of a two way stopcock. The ferric chloride was sublimed directly into five tubes which were attached in series to a 20 mm. glass tube. The system was again swept with dry nitrogen and each tube was removed separately by means of an oxygen flame. The crystals had a reddish brown coloration. The weight of ferric chloride used in the polymerizations was obtained indirectly by weighing a bottle before and after the ferric chloride was transferred from a tube.

Since the melting point of aluminum bromide is 97° , an all-glass, steam jacketed distillation apparatus, similar in principle to the apparatus used for stannic chloride³, was constructed. In this way the solid aluminum bromide could be purified by distillation and introduced into ampules.

Antimony pentachloride, C.P., (Eimer and Amend) was first used without purification in exploratory experiments. Ampules were prepared in a dry box in an atmosphere of nitrogen. The same procedure of filling the ampules was employed

here as for the titanium tetrachloride, except that the material was not distilled. In some experiments the compound was distilled but no effect on copolymer composition was detected, b.p. 72°/16 mm. (68°/14 mm.)⁶.

6) N. V. Sidgwick, "Chemical Elements and Their Compounds", Vol. I, Oxford University Press, Oxford, 1950, p. 794.

Trichloroacetic acid was distilled under reduced pressure and ampules were made using the method employed for the catalyst ampules. It was necessary, however, to keep the entire apparatus warm to prevent crystallization before the ampules were filled. Five batches of ampules were prepared and melting points of the samples were taken. The five melting points had a range of 58-59°(59.4°)⁷.

7) J. Kendall and P. M. Gross, THIS JOURNAL, 43, 1426 (1921).

Polymerization Technique.-

The polymerization technique used throughout was that described by reference 3, except for modifications employed with the use of a dry box. The copolymerizations are now carried out in an air tight, sheet metal dry box equipped with a glass window and rubber glove fittings. About 24 hours before each experiment the dry box containing a calcium chloride dish is flushed with dry nitrogen. Monomers and solvents are introduced into the reaction bottles through the manipulation of semi-micro and automatic burets respectively which are contained within the box. In this way it is possible to maintain a constant, reproducible atmosphere for each run.

Where cocatalysts were employed, the ampules were broken and the acid dissolved in the solution before the catalyst was added. In all experiments except those with antimony pentachloride and aluminum bromide in 1:1 carbon tetrachloride-nitrobenzene, the reaction was very fast. Due to the high dielectric constant of the medium employed, the reaction had to be stopped as soon as the catalyst was injected into the monomeric solution. The approximate time of most reactions was between five and ten seconds except those noted. This was the length of time required to remove the syringe from the bottle after adding catalyst, unscrew the cap of the polymerization bottle, and pour the solution into methanol.

All of the catalyst ampules were broken up by violent shaking and dissolved completely in the solvent mixture with the exception of aluminum bromide in carbon tetrachloride which remained as a partial solution.

On injecting aluminum bromide into the monomer mixture with pure carbon tetrachloride solvent, in a very short time the color turned from colorless to light orange to dark orange to red, ... the solution rapidly became warmer as the color darkened until boiling was noted. By precipitating the copolymer instantly after injection of aluminum bromide before any color change, it was possible to avoid any color change and heat effect.

Percent conversions were calculated from the weight of polymer obtained. The following formula was used in correct-

ing M_2 for conversions above 6%.

$$M_2 = M'_2 + \frac{M'_2 - m_2}{2} \times \text{conversion}$$

where M_2 and M'_2 are the corrected and uncorrected values, respectively, for the mole fraction of monomer 2 in the monomer mixture and m_2 is the mole fraction of monomer 2 in the polymer.

RESULTS AND DISCUSSION

Monomer Reactivity Ratios.-

The monomer reactivity ratios obtained in the system styrene, p-chlorostyrene in the various solvent systems employed are given in Table I. The experimental data are summarized in Table II. With all catalysts, preliminary experiments were carried out at 25-75 p-chlorostyrene-styrene ratios in order to obtain information as to reproducibility and an estimation of the rate. Most of these data are omitted for brevity but a representative group of experiments is summarized in Table III. As can be seen, good duplication of copolymer composition was obtained at low conversions. Typical copolymer composition curves are given in Fig. I. Since most of the copolymer composition curves are similar, they are omitted for brevity. The heterogeneous aluminum bromide system in carbon tetrachloride alone gave a small deviation and is represented in Fig. I. From Table I it can be seen that in all the homogeneous systems studied, the variation in the monomer reactivity ratios is small and within the range

of experimental error. The addition of trichloroacetic acid to titanium tetrachloride as a cocatalyst did not materially change the monomer reactivity ratios. This system has been studied by Plesch⁸ who has shown the cocatalyst activity of

8) P. Plesch, J. Chem. Soc., 543 (1950).

trichloroacetic acid with titanium tetrachloride. Thus it seems certain that in solvents of the range of dielectric constant employed here, the different anions from the catalyst-cocatalyst fragment does not appear to influence the ratios of the rates of addition of the ion pairs to the double bonds of the monomers in homogeneous solution.

Florin⁹ had reported that different Lewis acid catalysts

9) R. E. Florin, THIS JOURNAL, 71, 1867(1949); ibid, 73, 4468(1951).

for the system styrene, 3,4-dichlorostyrene in carbon tetrachloride affected the reactivity ratios markedly and explained his results with the mechanism proposed for cationic catalyzed polymerization reported by Fontana and Kidder¹⁰ for propylene in propane at low temperatures with an aluminum bromide-hydrogen bromide catalyst system. However, with the exception of stannic

10) C. M. Fontana and G. A. Kidder, ibid, 70, 3745 (1948).

chloride, his reported polymerizations were heterogeneous and his variations may be due to catalytic surface effects. It is entirely possible, however, that his system did show some variation due to the greater difference in reactivity between monomers of his pair.

It is again noted³ that variation in dielectric constant

from about 2.8 to 30 with a stannic chloride catalyst, Table I, footnote c, does not affect the monomer reactivity ratios. Values obtained in nitrobenzene are reported here. Likewise with titanium tetrachloride and aluminum bromide as catalysts, no variation in r_1 and r_2 is noted on change of dielectric constant in this system (Table I). Previously², it had been demonstrated that a change in concentration of stannic chloride from 0.5 to 2 mol percent in the system p-chlorostyrene- α -methylstyrene in carbon tetrachloride did not result in any change in copolymer composition. In Table II, data are presented to show that variation in titanium tetrachloride concentration from 1 to 3 mol percent in the styrene-p-chlorostyrene system in a 1:1 carbon tetrachloride-nitrobenzene solution gave no variation in copolymer composition.

The reactivity ratios and their probable errors were obtained by the use of a previously described procedure¹¹.

11) a. T. Alfrey, A. Goldberg and W.P. Hohenstein, ibid, 68, 2464 (1946).

b. "Copolymerization" by T. Alfrey, J.J. Bohrer and H. Mark, Interscience Publishers, Inc., New York, 1952.

Catalyst or Solvent Fragments.-

Control experiments using only polystyrene were carefully precipitated and purified. In no experiment with any of the solvent systems described in Table I, with ferric chloride, titanium tetrachloride, titanium tetrachloride-trichloroacetic acid and stannic chloride were any traces of chlorine or nitro-

gen detected in the polymers either by gravimetric analysis or infrared analysis¹². The infrared spectra were not entirely

12) We are grateful to Mr. Gerard Endres, one of our group, for infrared data on many samples of polystyrene prepared with stannic chloride as a catalyst.

satisfactory as negative evidence; however, coupled with the gravimetric results they indicated the absence of any measurable solvent or catalyst fragments in the polymer. Usually from 3 to 5 control polymers were subjected to rigorous purification and scrutiny¹³.

13) The method of chlorine analysis employed by Dr. Ritter is described by Pregl and Roth, "Quantitative Organische Mikroanalyse", Springer, 5th Edition, page 118. A sample of pure p-chlorostyrene gave a chlorine value of 25.40%; calcd. 25.58%. A sample of polystyrene prepared by catalysis with 2,2-azo-bis-isobutyronitrile in carbon tetrachloride gave values for chlorine of 0.52% and 0.45% showing good reproducibility with small quantities of chlorine present. Samples of polystyrenes prepared in bulk with benzoyl peroxide show the absence of any chlorine by this procedure as did all control experiments reported here with ionic catalysis. In this work alone we have had 24 analyses carried out in duplicate with surprisingly little variation. Dr. Ritter has informed us that he considers the method to have a range of accuracy of $\pm 0.2 \pm 0.3\%$ on these polymers. Larger samples are employed with these polymers than is usual for increased accuracy.

Thus, the copolymer compositions determined are not subject to errors due to incorporation of catalyst or solvent fragments. It is always possible that some termination may occur from the anionic cocatalyst fragment containing the metal by formation of an organo metallic bond which is hydrolyzed by precipitation with the polar solvent but this is unlikely. Number average molecular weights and kinetic evidence obtained in this laboratory further substantiate this conclusion.

Plesch has reported that the trichloroacetic acid fragment is found in the polymer when isobutylene is polymerized in hexane solution at -70° with a titanium tetrachloride-trichloroacetic acid catalyst (his polymers were precipitated in hexane and ethyl alcohol as solvents).

The behavior of antimony pentachloride is interesting. Here chlorine is introduced into the polymer in a 1:1 carbon tetrachloride-nitrobenzene solution confirming an earlier observation of Williams¹⁴ who found that antimony pentachloride when used as a catalyst for the polymerization of styrene in carbon tetrachloride appeared to act as a chlorinating agent. Determination of the monomer reactivity ratios for the styrene p-chlorostyrene system with antimony pentachloride in the solvent system indicated gave values of r_1 , 1.7 ± 0.2 ; r_2 , 0.55 ± 0.05 as a result of additional chlorine being added to the polymer.

Colclough¹⁵ has reported that no catalyst fragment containing antimony remains attached to the polymer chain when styrene is polymerised in nitrobenzene with radioactive antimony contained in an antimony pentachloride catalyst. Landler¹⁶ likewise has demonstrated that polystyrene prepared

14) G. Williams, J. Chem. Soc., 775 (1940).
15) R. O. Colclough, J. Polymer Sci., 5, 467 (1952)

16) Y. Landler, Rec. trav. chim. 68, 992 (1949).

in nitrobenzene solution with radioactive stannic bromide contains no bromine or radioactivity.

Preliminary experiments with silver nitrate in benzene-alcohol solutions with polystyrene, a copolymer of styrene and p-chlorostyrene, and the polymers prepared with an antimony pentachloride catalyst indicate that the aliphatic chloride structure is present.

Acknowledgment

We are grateful for the support of a portion of this work by the Office of Naval Research, Contract No. NR-356-262.

We are also grateful to Mr. Joseph Smith of the Bakelite Corporation for help in the interpretation of the infrared spectra.

Brooklyn, N.Y.

TABLE I

Effect of Variant Catalysts on Monomer Reactivity Ratios^a

<u>Catalyst^b</u>	<u>Reaction Medium</u>	<u>r₁</u>	<u>r₂</u>
SnCl ₄ ^c	nitrobenzene	2.2 ± 0.2	0.45 ± 0.02
TiCl ₄	nitrobenzene	2.2 ± 0.2	0.45 ± 0.02
AlBr ₃	nitrobenzene	2.3 ± 0.4	0.36 ± 0.05
TiCl ₄	nitrobenzene-carbon tetrachloride(1:1)	2.2 ± 0.2	0.45 ± 0.02
AlBr ₃	nitrobenzene-carbon tetrachloride(1:1)	2.0 ± 0.2	0.34 ± 0.05
SbCl ₅	"	1.7 ± 0.2	0.55 ± 0.05
FeCl ₃	nitrobenzene-carbon tetrachloride(1:4)	2.0 ± 0.1	0.43 ± 0.03
TiCl ₄ -CCl ₃ COOH ^d	nitrobenzene-carbon tetrachloride	2.0 ± 0.4	0.50 ± 0.05
AlBr ₃	carbon tetrachloride	1.51 ± 0.05	0.40 ± 0.02

a) All experiments carried out with styrene (M₁) and p-chloro-styrene (M₂) monomer mixtures. b) Concentration of catalysts was 1% based on monomers. c) Previously reported results³ in 50-50 carbon tetrachloride-nitrobenzene mixture; 0.5% stannic chloride based on monomers $r_1=2.10 \pm 0.2$; $r_2=0.35 \pm 0.02$; in pure carbon tetrachloride as solvent; 2% stannic chloride based on monomers; $r_1=2.5 \pm 0.4$; $r_2=0.30 \pm 0.03$. d) 1%- 0.5% catalyst-cocatalyst concentration respectively, based on monomers.

TABLE II

Copolymerization of Styrene (M_1) with p-Chlorostyrene (M_2) with Different Lewis Acids^a

<u>M_2 in monomer mixture^c</u>	<u>Conversion %</u>	<u>Cl, %^d</u>	<u>m_2</u>
<u>Stannic Chloride^b</u>			
0.243	7	4.30	0.132
.395	3	7.31	.232
.497	3	9.47	.307
.600	2	12.21	.408
.693	1	14.48	.496
.799	13	18.37	.657
<u>Titanium Tetrachloride^b</u>			
.506	16	10.50	.345
.613	14	12.84	.432
.694	9	14.83	.510
.791	9	18.18	.654
.252	20	4.63	.143
.427	34	8.30	.266
.517	36	10.66	.351
<u>Aluminum Bromide^b</u>			
0.201	8	2.79	0.085
.250	16	4.71	.140
.408	36	8.37	.268
.431	39	7.56	.240
.515	36	9.48	.308
.526	37	9.38	.302
.652	28	12.84	.431
.658	24	13.25	.447
.699	16	14.73	.505
.700	20	15.85	.550
.797	10	15.65	.545
.800	20	18.65	.670

TABLE II (continued)

<u>M₂ in monomer mixture^c</u>	<u>Conversion %</u>	<u>Cl, %^d</u>	<u>m₂</u>
<u>Titanium Tetrachloride^e</u>			
0.218	25	2.64	0.080
.323	12	5.91	.185
.455	8	8.52	.274
.530	16	10.72	.351
.622	6	11.63	.385
.715	6	15.31	.532
.820	8	17.87	.638
.906	4	21.51	.805
.702 ^f	11	15.16	.526
.791 ^f	7	17.09	.605
<u>Aluminum Bromide^e</u>			
0.207	10	3.85	0.118
.257	13	4.66	.143
.407	10	7.64	.244
.500	9	9.93	.323
.628	8	12.99	.433
.698	7	14.55	.498
.796	6	17.18	.605
<u>Ferric Chloride^g</u>			
0.205	13	4.02	0.123
.323	11	5.98	.188
.393	11	7.02	.222
.493	6	9.97	.326
.602	5	12.65	.424
.677	5	14.82	.513
.793	4	17.10	.607
.896	4	20.88	.776
<u>Titanium Tetrachloride-Trichloroacetic Acid^h</u>			
0.244	5	4.15	0.128
.398	5	7.63	.243
.503	7	10.58	.349
.594	4	13.08	.444
.698	8	16.02	.563
.796	4	17.80	.636

TABLE II (Continued)

<u>M₂ in monomer mixture^c</u>	<u>Conversion %</u>	<u>Cl, %^d</u>	<u>m₂</u>
<u>Aluminum Bromideⁱ</u>			
0.199	14	4.38	0.134
.246	16	5.45	.169
.401	10	8.68	.278
.500	12	10.94	.358
.634	9	13.94	.474
.697	10	15.53	.535
.798	9	18.41	.658

a) All experiments carried out at 0°C. b) In pure nitrobenzene as solvent; 1.0% catalyst concentration based on monomers. c) Corrected for finite conversions. d) Analyses by Dr. K. Ritter, Zurich, Switzerland. e) In a 1:1 carbon tetrachloride-nitrobenzene mixture as a solvent; 1.0% catalyst concentration based on monomers. f) In a 1:1 carbon tetrachloride-nitrobenzene mixture as a solvent; 3.0% catalyst concentration based on monomers. g) In a 1:4 nitrobenzene-carbon tetrachloride mixture as a solvent; 1.0% catalyst concentration based on monomers. h) In a 1:4 nitrobenzene-carbon tetrachloride mixture as a solvent; 1.0%, 0.5% catalyst-cocatalyst concentration respectively, based on monomers. i) In pure carbon tetrachloride as solvent; 1% catalyst concentration based on monomers.

TABLE III

Reproducibility of Copolymerization Experiments¹. Styrene
(M₁) 75 mole%; p-Chlorostyrene (M₂), 25 mole%

<u>Solvent</u>	<u>Catalyst</u>	<u>%Conversion</u>	<u>%Chlorine</u> ⁴	<u>m₂, mole%</u>
ØNO ₂	SnCl ₄	18	4.91	0.15
ØNO ₂	AlBr ₃	16	4.71	.15
ØNO ₂ /CCl ₄ ²	SnCl ₄	12	4.46	.14
ØNO ₂ /CCl ₄	AlBr ₃	13	4.66	.14
CCl ₄	SnCl ₄	14	4.13	.13
CCl ₄ ³	AlBr ₃	16	5.45	.17

1) Similar data were obtained for the other catalyst systems;

2) A 1:1 solution; 3) Heterogeneous solution; 4) Analyses

by Dr. K. Ritter, Zurich, Switzerland.

Fig. 1. Copolymerization of styrene (M_1) with p-chlorostyrene (M_2); 0, 1% ferric chloride in 1:4 nitrobenzene-carbon tetrachloride. $\bullet$, 1% aluminum bromide in carbon tetrachloride.

