ions, ionic micelles and lamellar micelles explains much of our data it is believed that the addition of alcohol is accompanied by other effects which contribute to the observed values. Prominent among these effects is the decreased hydration of the micelles occasioned by the lowered partial pressure of the water in the solvent. Since the bound water contained in both the ionic and lamellar micelles must be in equilibrium with the free water in the solvent, a lowering of the partial pressure of the latter will be attended by a loss of water from the micelles. This loss of water will result in increased mobilities which, in the case of ionic particles, will manifest itself in increased conductivities. Such an effect may contribute to the increased conductivities which result upon the addition of alcohol to concentrated aqueous solutions of dodecylammonium chloride and to the abnormal behavior of the more dilute solutions upon such additions. The lowered cationic transference values, however, indicate that this effect is not determinative as regards the general properties of the system.

That the composition of the lamellar micelle is influenced by external factors has been shown recently by Ross and McBain[16] who observed marked increases in the long spacings of hexanolamine oleate upon dilution as shown by X-rays, their results thus confirming those previously reported upon soap solutions.[17] Contemporaneously with this work Harkins, Mattoon and Corrin[18] published an extensive investigation of the structure of soap micelles as shown by X-rays. Their results also confirmed that the long spacing is a function of the concentration, the spacing increasing materially upon lowering the concentration. It has been observed that the addition of salt to a solution of a colloidal electrolyte brings about a decrease in the specific conductivity attributable to the colloidal electrolyte and is also attended by a shift in the critical point toward a *lower* concentration.[19] Such observations are, however, not antagonistic to our findings since the addition of salt is undoubtedly attended by a decrease in hydration of the micelles. On the other hand, the presence of an electrolyte and the common ion effect must greatly reduce ionization and favor the formation of associated molecules as evidenced by the shift in critical concentration.

Summary

The electrical behavior of hexyl- and dodecylammonium chlorides in pure water, pure ethanol and in various concentrations of aqueous ethanol has been studied.

The addition of ethanol to aqueous solutions of hexylammonium chloride lowers the conductivities at all concentrations investigated. The conductivities of concentrated solutions of dodecylammonium chloride are increased by the addition of small amounts of alcohol. The addition of alcohol to more dilute aqueous solutions of this salt is accompanied by an irregular decrease in the conductivities.

Micelle formation is completely inhibited by the addition of large amounts of alcohol to aqueous solutions of dodecylammonium chloride.

The difference in behavior of these two salts has been ascribed to micelle formation in solutions of dodecylammonium chloride. The behavior of these salts in such solvents has been discussed in the light of the present micelle theory

CHICAGO, ILLINOIS RECEIVED APRIL 22, 1946

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[16] Ross and McBain, THIS JOURNAL, **68**, 296 (1946).

[17] References to this work are given by Ross and McBain.[16]

[18] Harkins, Mattoon and Corrin, *ibid.*, **69**, 220 (1946).

[19] Wright, Abbott, Sivertz and Tartar, *ibid.*, **61**, 549 (1939).

[CONTRIBUTION FROM THE POLYTECHNIC INSTITUTE OF BROOKLYN]

Copolymerization of Vinyl Compounds with Dienes[1]

BY TURNER ALFREY, JR., A. I. GOLDBERG AND W. P. HOHENSTEIN

When two vinyl monomers (A and B) are polymerized together, the composition of the resulting copolymer has been shown theoretically and experimentally,[2] to be governed by a "copolymer composition equation" of the form

$$\frac{b}{a} = \frac{B}{A}\,\alpha\,\frac{\beta B + A}{\alpha B + A}$$

where b and a are the molar proportions of the respective monomer groups in the initial copolymer, B and A are the molar proportions of the monomers in the monomer mixture, and α and β are ratios of rate constants for chain propagation

$$\alpha = k_{ab}/k_{aa},\ \beta = k_{bb}/k_{ba}$$

In this investigation the copolymerization of styrene with chloroprene and dichlorostyrene with styrene has been studied.

Experimental

Monomers.—Styrene, Dow N99, was washed, dried and distilled *in vacuo*; 2,5-dichlorostyrene, Monsanto, was washed with dilute alkali, water, and dried over calcium chloride; chloroprene (2-chlorobutadiene-1,3), du Pont,

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[1] This paper is from the doctoral dissertation submitted by A. I. Goldberg to the Polytechnic Institute of Brooklyn and was presented in part at the Atlantic City Meeting of the American Chemical Society, April, 1946.

[2] (a) Alfrey and Goldfinger, *J. Chem. Phys.*, **12**, 205 (1944); (b) Mayo and Lewis, THIS JOURNAL, **66**, 1594 (1944); (c) Wall, *ibid.*, **66**, 2050 (1944); (d) Alfrey, Merz and Mark, *J. Polymer Research*, **1**, 37 (1946); (e) Lewis, Mayo and Hulse, THIS JOURNAL, **67**, 1701 (1945); (f) Alfrey and Harrison, *ibid.*, **68**, 299 (1946).

was distilled *in vacuo* from solution and redistilled *in vacuo*, refractive index 1.460; butadiene-1,3, Matheson Co., technical, was condensed at Dry Ice temperatures. The chlorinated monomers polymerize very rapidly and were used within forty-eight hours after purification. All monomers were stored at −10° before use.

Procedure and Results.—The polymerizations were carried out in sealed tubes of 50 cc. capacity at 70° with 0.1% benzoyl peroxide catalyst dissolved in 25 g. of the monomer mixture. Monomer ratios were varied from about 10 to 90 mole per cent. The tubes were sealed and the polymerization was carried out until a noticeable rise in viscosity was observed. They were then cooled and opened, and the contents were poured into 3-4 volumes of methanol. The purified polymers were isolated by the frozen benzene method of Lewis and Mayo[3] and dried in a vacuum oven at 55° for 2-3 days at 3 mm. pressure until constant weight was obtained. The samples were analyzed for chlorine and the results of the analysis are given in Tables I and II.

TABLE I

BULK COPOLYMERIZATION OF STYRENE (A) AND CHLOROPRENE (B) AT 70°[a]

Momomer		Polymer			
Mole fraction B	Reaction time, hr.	Yield, %	Chlorine, %		Mole fraction B
0.093	4.5	6.7	20.1	21.3	0.555
.245	4.5	9.5	29.0	29.0	.755
.432	1.58	1.8	33.6	32.4	.845
.622	1.83	4.0	36.3	35.7	.912
.756	1.83	5.4	36.4	37.1	.928
.889	1.83	5.8	38.4	38.0	.959
.111	2.25	1.6	18.9	18.9	.513
.271	2.17	2.7	28.2	28.2	.736
.421	2	4.5	32.2	32.2	.827
.618	1	5.4	32.4	33.2	.840
.766	1.5	3.3	37.0	37.4	.938
.900	1.5	2.8	38.5	38.7	.967

[a] In presence of 0.1 weight per cent. of benzoyl peroxide.

TABLE II

BULK COPOLYMERIZATION OF 2,5-DICHLOROSTYRENE (A) AND 1,3-BUTADIENE (B) AT 70°[a]

Monomer		Polymer			
Mole fraction B	Reaction time, hr.	Yield, %	Chlorine, %		Mole fraction B
0.126	0.75	2.26	35.50	35.34	0.330
.208	1.25	1.13	33.95	34.08	.396
.247	1.5	3.5	34.66	34.70	.368
.358	1.8	6.55	30.86	30.99	.510
.675	15	7.2	24.99	24.75	.675
.823	8	2.5	18.35	18.27	.798
.906	16	3.0	12.16	12.28	.883
.968	48	5.0	5.50	5.45	.954

[a] In presence of 0.1 weight per cent. of benzoyl peroxide.

The constant composition copolymerizing mixture of dichlorostyrene-butadiene was polymerized to varying degrees of conversion. In this case the dichlorostyrene was weighed into an Erlenmeyer flask with a side arm and the added catalyst was dissolved. Excess butadiene, redistilled at −4°, was added and allowed to evaporate until the proper weight was reached. The solution was rapidly cooled to −40° and aliquot portions were weighed into individual tubes which were cooled in Dry Ice. The tubes were sealed and then accurately weighed. The polymerization, purification and isolation was carried out as described above. The rubbery polymers were dissolved in toluene, and viscosity and osmotic pressure data were secured (see Table III). Viscosities were measured with 2-cc. Ostwald pipets and the osmotic measurements were made with the semi-micro osmometer of Zimm and Meyerson[4] using the static method.

Discussion

Figure 1 shows the experimental results obtained for the system styrene (A)-chloroprene (B). The *average* mole fraction of chloroprene in the monomer, computed from conversion data, was used. The copolymers darkened on standing and the odor of hydrogen chloride was noted, a loss of 2 mole per cent. of the chlorine being indicated by the fact that the composition curve extrapolated to 98 mole per cent. chloroprene for the polymer containing no styrene. Corrected values, taking this loss into account, are shown.

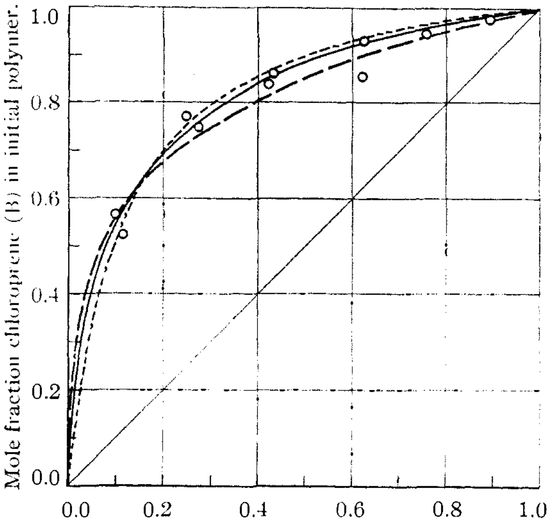

Fig. 1.—Copolymer composition curve for the system styrene (A)-chloroprene (B): - - - - - - $\alpha = 10$, $\beta = 9$; — $\alpha = 20$, $\beta = 7$; — — — $\alpha = 40$, $\beta = 5$.

The theoretical curve for α equal to 20 and β equal to 7 gives the most satisfactory fit. The curves for α equal to 40 and β equal to 5 and for α equal to 10 and β equal to 9 are also shown and serve to show the limits of the possible values. This variation in the reactivity ratios is an indication of the precision of these values. The central portion of a composition curve of this type is extremely insensitive to the value of α chosen. In order to evaluate α accurately it is necessary to have experimental points which lie fairly close to zero mole per cent. chloroprene in the copolymer. The value of β is known with greater precision, due to the nature of the copolymerization curve. The values of α and β, 20 ± 10 and 7 ± 2, respectively, indicate that chloroprene monomer adds 20 times as fast to a styrene radical as does styrene monomer, and 7 times as fast to a chloroprene radical.

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[3] Lewis and Mayo, *Ind. Eng. Chem., Anal. Ed.*, **17**, 134 (1945).

[4] Zimm and Meyerson, THIS JOURNAL, **68**, 911 (1946)

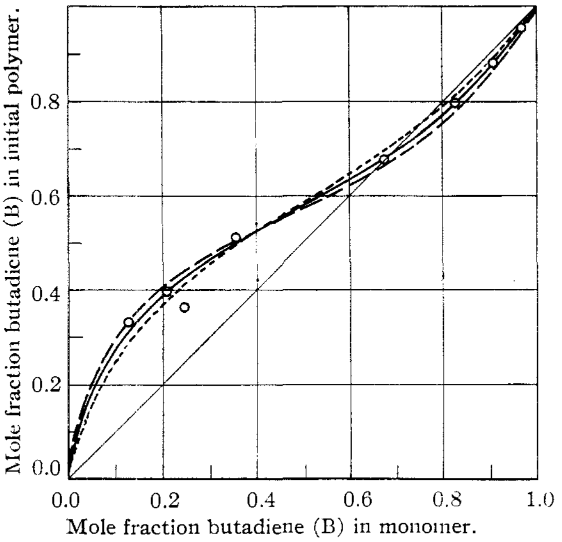

Fig. 2.—Copolymer composition curve for the system dichlorostyrene (A)-butadiene (B): ----- $\alpha = 4$, $\beta = 0.75$; — $\alpha = 5$, $\beta = 0.65$; —·—·— $\alpha = 6$, $\beta = 0.55$.

Figure 2 shows the composition curve for the system 2,5-dichlorostyrene–butadiene, which is quite different in nature from that for the styrene-chloroprene system. The best values of α and β were found to be 5.0 ± 1 and 0.65 ± 0.1, respectively. This indicates that butadiene monomer adds about 5 times as fast to a dichlorostyrene radical as does dichlorostyrene monomer. On the other hand, butadiene monomer adds only 0.65 times as fast to a butadiene radical as does dichlorostyrene monomer. At low butadiene concentrations the copolymer is richer in dichlorostyrene than the monomer mixture; the point at which the initial polymer has the same composition as the monomer mixture occurs at about 68 mole per cent. of butadiene. Between 60 and 100 mole per cent. (30 and 100 weight per cent.) butadiene, the copolymer composition deviates no more than three mole per cent. from that of the monomer mixture. The reported precision of the α and β values for this system follows from an analysis similar to the previous one.

The monomer reactivity ratios for the system styrene-butadiene have been evaluated by Mayo[5] and are as follows:

$$\alpha = 1/\sigma = 1.3$$
$$\beta = \mu = 1.4$$

Butadiene is about $^4/_3$ as reactive as styrene toward either radical type. Thus this system appears to lie between the two reported above.

The general over-all reactivity of the above two systems is of interest. In Figs. 3 and 4 the initial conversion in terms of per cent. per hour is plotted against mole fraction diene. There is a marked change in the dichlorostyrene–butadiene polymerization rate as the monomer ratio is varied. With dichlorostyrene polymerization is substantially complete in two to three hours under these conditions, whereas 100% butadiene is only about 2% polymerized in one-hundred hours. The styrene–chloroprene system shows a much smaller variation in initial per cent. conversion as the monomer ratio is changed. Chloroprene itself polymerizes from 3 to 5 times as fast as 100% styrene. It is noteworthy that the former system, which has such a marked difference in individual monomer rates, forms a comparatively homogeneous copolymer whereas the latter system, whose monomers have similar rates, forms a relatively non-homogeneous copolymer.

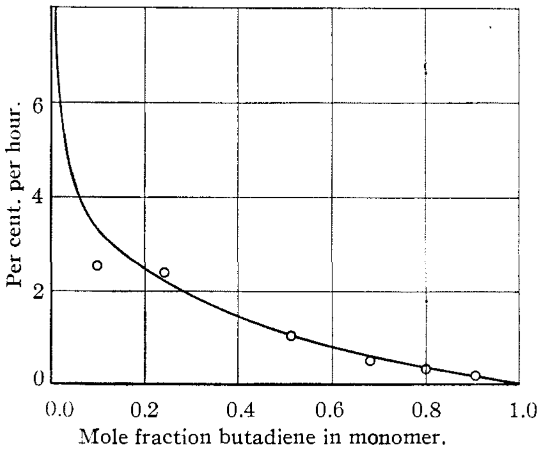

Fig. 3.—Initial rate of conversion of the dichlorostyrene–butadiene copolymer system.

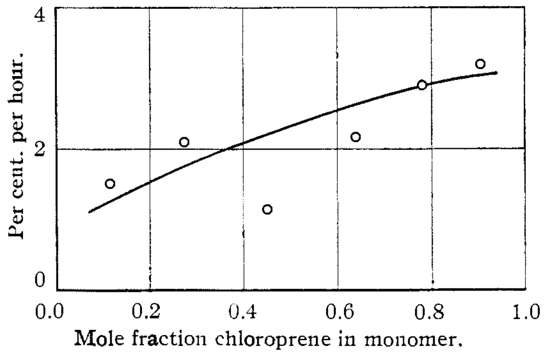

Fig. 4.—Initial rate of conversion of the styrene–chloroprene copolymer system.

Constant Copolymerizing Mixture.—In the copolymerization of a diene and an olefin, it is generally observed that the polymer becomes partially insoluble as the degree of conversion becomes large. It was desirable to study the change in molecular weight of such a copolymer system under conditions where the chemical composition of the copolymer remains constant as the polymerization proceeds. The dichlorostyrene–butadiene system provides such a monomer mixture at 68 mole per cent. of butadiene, Table III. At slightly above 30% conversion some signs of insolubility arose and the reaction was not carried further. The constancy of the co-

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(5) Mayo, personal communication.

TABLE III

CONSTANT COPOLYMERIZATION MIXTURE[a]

60.6 wt.% dichlorostyrene, 39.4 wt.% butadiene

Reaction time, hr.	Yield, %	[η] at 30°	k'	$\overline{M}_n \times 10^3$	μ at 27°	Polymer Chlorine, %		Polymer Dichlorostyrene, %
15	7.2	0.64_2	0.36_4	90	0.42_1	24.99	24.75	60.7
25	11.6	$.66_6$	$.34_7$	100	$.40_4$	...	...	..
47	17.6	$.72_5$	$.36_4$	130	$.39_7$	...	...	..
57	31.4	$.89_0$	$.35_1$	160	$.39_5$	24.39	24.25	59.4

[a] In presence of 0.1 weight per cent. of benzoyl peroxide at 70°.

polymer composition is shown by the analytical results secured at the 7.2 and 31.4% extremes of conversion. The intrinsic viscosities were measured, and were found to remain relatively constant up to about 12% conversion and then showed a marked rise, a 40% increase being found at 31% conversion. A similar set of measurements with dichlorostyrene alone showed that the intrinsic viscosities were constant up to 21.0% conversion, the intrinsic viscosity being 0.77 ± 0.03. The number average osmotic molecular weights of the copolymers were determined and ranged from 90,000 to 160,000, increasing with degree of conversion. The viscosity, k', and osmotic pressure, μ, constants[6] indicate, among other properties, the shapes and flexibilities of the polymer in the solvent, toluene; they were found to be constant within experimental error.

Acknowledgment.—The authors wish to express their appreciation to the Dow, Monsanto and du Pont companies for the monomer samples; to Dr. Carl Tiedcke for micro-analyses of the butadiene copolymers, and to Miss Doris Linberg for her assistance in much of the laboratory work.

Summary

Experimental results on two olefin–diene copolymer systems show that the simple copolymer composition equation is obeyed. The values of α and β for the systems styrene–chloroprene, and dichlorostyrene–butadiene have been determined. An investigation was made of the change in viscosity and molecular weight with increasing degree of conversion of the constant copolymerizing mixture of the latter system.

(6) Huggins, *Ind. Eng. Chem.*, **35**, 216 (1943); *J. Phys. Chem.*, **42**, 911 (1938); **43**, 439 (1939).

BROOKLYN, N. Y. RECEIVED MAY 27, 1946

[CONTRIBUTION FROM THE RESEARCH LABORATORY, GENERAL ELECTRIC COMPANY]

The Preparation and Polymerization of Vinyl Fluoride

BY A. E. NEWKIRK

The polymerization of vinyl fluoride has been reported to be difficult or impossible.[1,2,3] There seemed to be no theoretical basis for this difficulty, and as the polymer should have useful properties an investigation was undertaken to prepare and polymerize vinyl fluoride.

Preparation of Vinyl Fluoride

Vinyl fluoride was prepared first by Swarts[4] by the reaction between 1,1-difluoro-2-bromoethane and zinc. This general reaction between an active metal and a halogenated ethane has been used by other investigators for the preparation of vinyl fluoride.[5,6,7,8] Swarts[9] has also used phenylmagnesium bromide in ether, and alcoholic potassium iodide, in place of the metal for removing halogen. The reaction of vinyl chloride or bromide with a metal fluoride is not described in the literature, and was tried with but slight success. Vinyl fluoride has been prepared by the addition of hydrogen fluoride to acetylene both without a catalyst[10,11,12], and with the aid of mercury (II) oxide on activated carbon.[13]

The catalytic reaction in the vapor phase over catalysts of mercury (II) chloride, or mixtures of this and barium chloride, supported on active carbon was used to prepare vinyl fluoride for the polymerization experiments. The latter catalyst was superior in all respects. It gave higher conversions, permitted higher space velocities, and had longer life. Typical results are shown in Table I. The mercury (II) chloride catalyst was active for from eight to twenty-four hours, after which its activity dropped to zero. Globules of mercury were observed in the spent catalyst.

The crude gas from the reactor, after removal of hydrogen fluoride, was mixed with ethane and fractionally distilled at atmospheric pressure in a low-temperature column. The addition of ethane permitted the removal of acetylene as an azeotrope.[14] The vinyl fluoride fractions had a purity

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(6) A. L. Henne and T. Midgley, Jr., THIS JOURNAL, **58**, 882 (1936).

(7) A. L. Henne, *ibid.*, **60**, 2275 (1938).

(8) P. Torkington and H. W. Thompson, *Trans. Faraday Soc.*, **41**, 236 (1945).

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(12) A. L. Henne, "Organic Reactions," Vol. 2, John Wiley and Sons, New York, N. Y., 1944, p. 66.

(13) J. Söll, German Patent 641,878 (1937), British Patent 469,421 (1937), U. S. Patent 2,118,901 (1938).

(14) W. A. McMillan, THIS JOURNAL, **58**, 1345 (1936).