[CONTRIBUTION FROM THE CENTRAL RESEARCH DEPARTMENT, MONSANTO CHEMICAL COMPANY]

Copolymerization. IV. The Validity of the Tripolymer Equation for the Systems: Styrene–Vinyl Chloride–Methyl Acrylate and Styrene–Vinyl Chloride–Acrylonitrile

BY EARL C. CHAPIN, GEORGE E. HAM AND REID G. FORDYCE

The theory of the propagation step in copolymerizations developed by Alfrey and Goldfinger,[1] Mayo and Lewis[2] for two components was later extended to three component systems by Alfrey and Goldfinger[3] and finally to the more general case of *n* monomers by Walling and Briggs.[4] While a considerable amount of experimental data has been reported for two-component systems,[2,5–11] apart from the original experiments of Walling and Briggs[4] further experimental confirmation of the tripolymer equation has been lacking. It is the purpose of this paper to present additional copolymerization rate data in order to test the applicability of the tripolymer equation to systems other than those described by Walling and Briggs. It is also our purpose to present data based on tripolymer samples isolated at low conversions where the simple differential form of the tripolymer equation can be employed for direct comparison with experimental results.

The systems vinyl chloride–styrene–methyl acrylate and vinyl chloride–styrene–acrylonitrile were chosen since the tripolymer composition could be determined with accuracy by analysis. Thus chlorine, carbon and hydrogen analyses on products from the former system, and chlorine and nitrogen analyses on tripolymers from the latter system were sufficient to define the relative proportions of combined comonomers in each case.

The monomer reactivity ratios for the systems styrene–methyl acrylate[7] and styrene–acrylonitrile[5,10] have been reported. Since the tripolymer equation involves the monomer reactivity ratios of the three separate two component systems involved, it was necessary to determine first, monomer reactivity ratios for the systems, styrene–vinyl chloride, vinyl chloride–methyl acrylate and vinyl chloride–acrylonitrile. These data were then used to predict the compositions of tripolymers produced from different compositions of the three component systems cited above. Experimental data comparing the actual compositions with the calculated values were then obtained.

In determining the monomer–polymer composition curves for the three two-component systems, copolymerizations were allowed to proceed to low conversions (mainly <4%) and the initial product was isolated and purified. The amount of combined vinyl chloride was determined in all cases by chlorine analyses. Likewise for the tripolymer experiments, products at low conversions (mainly <4%) were isolated, purified and analyzed as indicated above.

Results and Discussion

The shapes of the monomer–polymer composition curves for the system vinyl chloride–styrene determined by solution and by emulsion polymerization are shown in Figs. 1 and 2, respectively. The experimental data are summarized in Table I. The following monomer reactivity ratios[12] gave the best curve fit to the data obtained:

	Solution polymerization	Emulsion polymerization
Styrene	35	35
Vinyl chloride	0.067	0.077

TABLE I

VINYL CHLORIDE–STYRENE COPOLYMERIZATIONS

Monomer mole % styrene	Time at polymerization temp., hours	Wt. % conversion	Chlorine Analyses I	Chlorine Analyses II	Copolymer mole % styrene
Solution polymerization, acetone, 48°, 0.5% Bz_2O_2					
83.6	18.2	3.0	0.31	0.32	99.0
71.6	24.0	2.6	.48	.52	98.5
60.6	24.0	4.4	1.00	1.00	97.2
49.6	24.0	4.0	1.12	1.16	96.7
38.8	24.0	2.0	1.35	1.79	95.5
13.1	67.0	4.0	6.87	7.27	80.9
9.9	166.0	1.2	9.06	9.14	76.0
7.6	239.5	4.6	14.79	15.17	62.8
3.2	339.5	3.6	35.27	35.33	26.8
Emulsion polymerization, 50°, 0.5% H_2O_2					
88.6	6.0	2.0	0.40	...	98.8
78.4	46.0	3.0	.63	0.99	98.6
58.9	46.0	1.0	1.62	...	95.3
39.7	70.0	1.9	3.17	...	91.0
9.7	70.5	0.6	16.18	16.55	59.8

In accordance wth arguments previously advanced,[10,11] the close proximity of the two curves shows that an oil-phase mechanism of emulsion polymerization is operative for this system. The data also show that styrene monomer has a much greater tendency than vinyl chloride to add either to a styrene free radical or to a vinyl chloride free

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[1] Alfrey and Goldfinger, *J. Chem. Phys.*, **12**, 205 (1945).

[2] Mayo and Lewis, THIS JOURNAL, **66**, 1594 (1944).

[3] Alfrey and Goldfinger, *J. Chem. Phys.*, **12**, 322 (1945).

[4] Walling and Briggs, THIS JOURNAL, **67**, 1774 (1945).

[5] Lewis, Mayo and Hulse, *ibid.*, **67**, 1701 (1945).

[6] Alfrey and Lavin, *ibid.*, **67**, 2044 (1945).

[7] Alfrey, Merz and Mark, *J. Polymer Research*, **1**, 37 (1946).

[8] Alfrey and Goldfinger, *J. Chem. Phys.*, **14**, 115 (1946).

[9] Alfrey, Goldberg and Hohesnstein, THIS JOURNAL, **68**, 2464 (1946).

[10] Fordyce and Chapin, *ibid.*, **69**, 581 (1947).

[11] Fordyce and Ham, *ibid.*, **69**, 695 (1947).

[12] The constants reported in this paper represent the ratio of the rate constants for the reaction of the given radical with the corresponding monomer and with the other monomer, respectively. The values correspond to the r_1 and r_2 nomenclature of Alfrey, Mayo and Wall, *J. Polymer Science*, **1**, 581 (1946).

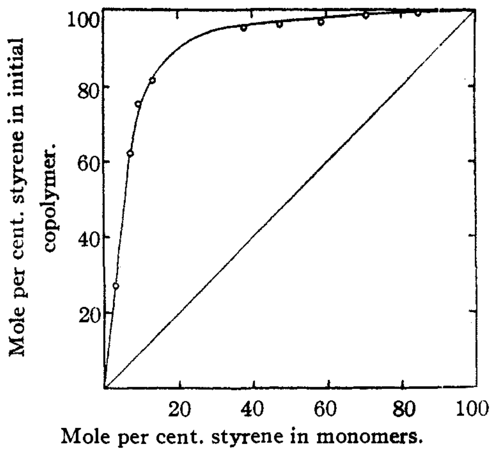

Fig. 1.—Monomer–polymer composition curve for the system vinyl chloride–styrene solution polymerization.

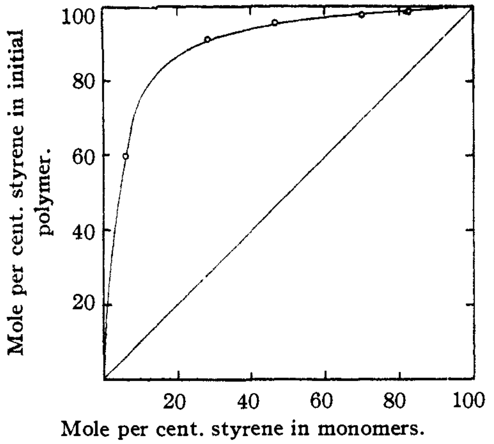

Fig. 2.—Monomer–polymer composition curve for the system vinyl chloride–styrene emulsion polymerization.

radical. Hence styrene–vinyl chloride batch copolymerizations carried to completion must necessarily produce samples highly heterogeneous with respect to composition. Inspection of the polymerization times required (Table I) shows that styrene–vinyl chloride copolymers do not form readily and copolymerize at a much slower rate than either constituent alone.

TABLE II

VINYL CHLORIDE–METHYL ACRYLATE COPOLYMERIZATIONS

Monomer mole % methyl acrylate	Time at polymerization temp., hours	Wt. % conversion	Chlorine analyses I	Chlorine analyses II	Copolymer mole % methyl acrylate
Mass polymerization, 50°, 0.05% Bz_2O_2					
7.5	7.0	1.7	27.12	27.32	44.1
15.4	6.0	3.0	13.30	13.75	69.9
23.7	4.0	5.9	10.84	10.94	75.3
32.6	7.0	2.2	7.24	7.61	82.8
42.1	7.5	4.0	5.69	5.98	86.4
52.1	7.5	4.1	4.00	4.45	90.0
74.4	12.0	4.5	1.18	1.50	96.8
86 7	16 0	4.6	0.68	0.76	98.3

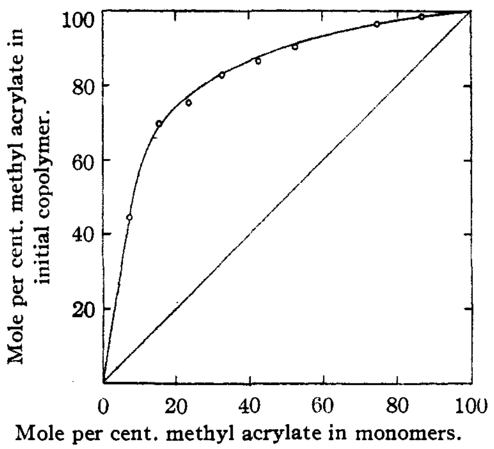

Fig. 3.—Monomer–polymer composition curve for the system vinyl chloride–methyl acrylate, mass polymerization.

The monomer–polymer composition curve for the system vinyl chloride–methyl acrylate copolymerized in mass is shown in Fig. 3, and the experimental data for this series of experiments are given in Table II. The monomer reactivity ratios for the two free radicals were found to be: vinyl chloride 0.083, methyl acrylate 9.0.

The relationship of monomer composition to copolymer composition for the system vinyl chloride–acrylonitrile determined in solution is represented in Fig. 4. The experimental data from which this curve[13] was drawn are given in Table III. The monomer reactivity ratios giving a good curve through the experimental points were found to be: vinyl chloride 0.074 and acrylonitrile 3.7.

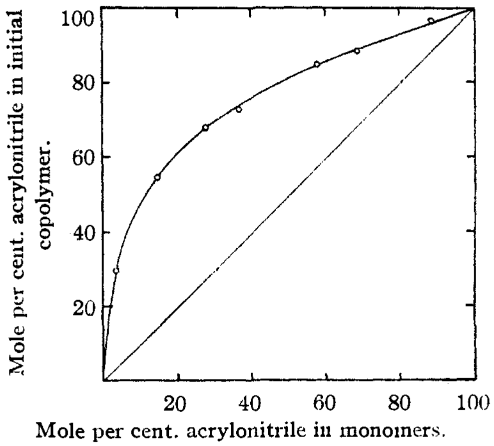

Fig. 4.—Monomer–polymer composition curve for the system vinyl chloride–acrylonitrile solution polymerization.

The monomer reactivity ratios reported above were determined by varying their values in the copolymer equation until a good curve through

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[13] After completing this manuscript, U. S. Patent 2,420,330 by Shriver and Fremon was issued, showing a similar curve for this system.

TABLE III

VINYL CHLORIDE–ACRYLONITRILE COPOLYMERIZATIONS

Monomer mole % acrylonitrile	Time at polymerization temp., hours	Wt. % conversion	Chlorine analyses I	Chlorine analyses II	Copolymer mole % acrylonitrile
Solution polymerization, acetone, 50°					
4.0	20^a	5.0	41.89	42.07	29.4
14.5	14^b	<4.0	28.14	28.14	54.5
27.8	14^b	<4.0	20.13	20.21	68.0
36.3	14^b	<4.0	17.29	17.45	73.6
57.5	20^a	6.0	9.86	9.87	85.0
68.5	14^a	0.5	7.57	7.57	88.4
88.5	14^a	4.0	2.16	2.47	96.5

^{a} 0.5 wt. % Bz_2O_2. ^{b} 0.7 wt. % Bz_2O_2.

the experimental points was obtained. It is difficult, by this method, to define the limits of accuracy of the values since the curve fit is a matter of opinion. For example, relatively small changes in the r_1, r_2 values for the systems vinyl chloride–methyl acrylate and vinyl chloride–acrylonitrile result in curves which do not pass through the experimental points at all. The parameters reported for these systems, therefore, are probably accurate to within at least 10%. On the other hand, the monomer reactivity ratios for the system styrene–vinyl chloride must be considered to be less accurate. Relatively large changes in the r_1, r_2 values of this type of curve (large r_1—small r_2 values) do not result in a marked alteration of the curve shape. Moreover, the curve fit technique for a system of this type gives undue emphasis to certain experimental points, particularly in the region where the curve "breaks." Consequently, small analytical errors for such points produce considerable changes in the r_1 and r_2 values obtained by curve-fitting.

The Alfrey and Goldfinger equations[3] for predicting the initial polymer composition from a monomeric mixture of three components are of the form

$$\frac{d[M_1]}{d[M_2]} = \frac{\frac{[M_1][M_2]}{r_{21}r_{32}} + \frac{[M_1]}{r_{31}}\left(\frac{[M_1]}{r_{21}} + \frac{[M_3]}{r_{23}}\right)}{\frac{[M_1][M_2]}{r_{12}r_{31}} + \frac{[M_2]}{r_{32}}\left(\frac{[M_3]}{r_{12}} + \frac{[M_3]}{r_{13}}\right)} \cdot \frac{[M_1] + \frac{[M_2]}{r_{12}} + \frac{[M_3]}{r_{13}}}{[M_2] + \frac{[M_1]}{r_{21}} + \frac{[M_3]}{r_{23}}}$$

$$\frac{d[M_1]}{d[M_3]} = \frac{\frac{[M_1][M_2]}{r_{21}r_{32}} + \frac{[M_1]}{r_{31}}\left(\frac{[M_1]}{r_{21}} + \frac{[M_3]}{r_{23}}\right)}{\frac{[M_1][M_3]}{r_{13}r_{21}} + \frac{[M_3]}{r_{23}}\left(\frac{[M_2]}{r_{12}} + \frac{[M_3]}{r_{13}}\right)} \cdot \frac{[M_1] + \frac{[M_2]}{r_{12}} + \frac{[M_3]}{r_{13}}}{[M] + \frac{[M_1]}{r_{31}} + \frac{[M_2]}{r_{32}}}$$

where $[M_1]$, $[M_2]$ and $[M_3]$ represent monomer concentrations of the three components, $d[M_1]$, $d[M_2]$ and $d[M_3]$ represent the amounts of combined comonomers, respectively, in the polymer molecules first formed, and r_{12}, r_{21}, r_{13}, r_{31}, r_{23} and r_{32} are the monomer reactivity ratio parameters for the three two component systems involved, as defined recently by Alfrey, Mayo and Wall.[12]

Experimental data for the system styrene (M_1)–methyl acrylate (M_2)–vinyl chloride (M_3) are given in Table IV. Utilizing data previously published,[5,7,10] together with the monomer reactivity ratios reported above, the following values were used to predict polymer composition for this system: $r_{12} = 0.75$, $r_{13} = 35$, $r_{21} = 0.20$, $r_{23} = 9.0$, $r_{31} = 0.067$ and $r_{32} = 0.083$. A comparison of the predicted composition with the composition actually obtained is given

	Initial monomer composition	Weight per cent. Predicted polymer composition	Polymer composition by analysis
Styrene	20	45.2	47.6
Methyl acrylate	60	53.7	52.0
Vinyl chloride	20	1.1	1.3
Styrene	60	75.7	76.1
Methyl acrylate	20	23.6	22.8
Vinyl chloride	20	0.7	1.1

Similarly, the experimental data for the system styrene (M_1)–acrylonitrile (M_2)–vinyl chloride (M_3) are given in Table IV, and the following parameters were employed in calculating polymer composition: $r_{12} = 0.41$, $r_{13} = 35$, $r_{21} = 0.04$, $r_{23} = 3.7$, $r_{31} = 0.067$ and $r_{32} = 0.074$. The following results were obtained for this system

	Initial monomer composition	Weight per cent. Predicted polymer composition	Polymer composition by analysis
Styrene	32.0	66.1	67.1
Acrylonitrile	48.8	33.4	32.5
Vinyl chloride	19.2	0.5	0.4
Styrene	30.2	71.0	70.4
Acrylonitrile	15.4	26.8	26.2
Vinyl chloride	54.4	2.2	3.4

Agreement between the predicted and actual compositions shown above provides support for the monomer reactivity ratios reported and tends to confirm the validity of predictions based on the tripolymer equations.

Experimental

Vinyl Chloride Monomer.—Redistilled Dow Chemical Co. material was used for all experiments.

Styrene Monomer.—Redistilled Dow Chemical Co. N-100 material was used for all experiments.

Acrylonitrile.—Redistilled American Cyanamid Co. material was used.

Methyl Acrylate.—Redistilled Rohm & Haas material was used.

Benzoyl Peroxide.—The product of the Lucidol Corp. was used.

Acetone.—Redistilled material from the Commercial Solvents Corp. was employed.

Vinyl Chloride–Styrene Copolymerizations

Solution.—A solution comprising 50 g. of acetone and 50 g. of total monomer was taken for all experiments. Appropriate amounts (Table I) of styrene, acetone and benzoyl peroxide weighed into a 200-ml. pressure bottle were gradually cooled in a Dry Ice-bath to −50°. A suitable volume of liquid vinyl chloride also cooled to Dry Ice temperatures was added. A metal cap with tinfoil liner was tightly screwed on the bottle which was allowed to warm to room temperature and weighed.

TABLE IV

TRIPOLYMER MASS POLYMERIZATIONS

Monomer	wt. %	Temp., °C.	Time, hours	Wt. % conversion	Analyses	Polymer wt. %
Vinyl chloride	20				C, 72.40, 72.79	1.5
Styrene	20	50	5.3[a]	3.0	H, 7.66, 7.84	46.5
Methyl acrylate	60				Cl, 0.74, 0.74	52.0
Vinyl chloride	20				C, 83.28, 83.41	1.2
Styrene	60	50	4[a]	2.3	H, 7.66, 7.72	76.0
Methyl acrylate	20				Cl, 0.55, 0.65	22.8
Vinyl chloride	19.2	50	5[b]	2.7	N, 8.57, 8.61	0.35
Styrene	32.0	25	48		Cl, 0.24, 0.25	67.1
Acrylonitrile	48.8					32.5
Vinyl chloride	54.4	50	11[b]	5.0	N, 6.93, 6.94	3.4
Styrene	30.2	25	48		Cl, 1.87, 1.97	70.4
Acrylonitrile	15.4					26.2

[a] 0.05 wt. per cent. Bz_2O_2. [b] 0.2 wt. per cent. Bz_2O_2.

Vinyl chloride added was determined by difference. The bottle was rotated end-over-end in a constant temperature water-bath regulated to 48 ± 0.05°. When a slight increase in viscosity was observed the bottle was removed, cooled to room temperature and weighed. Weight losses during the polymerization averaged 0.1–0.2 g. A mean value was taken for vinyl chloride concentrations during the polymerization, assuming total loss to be vinyl chloride monomer. The metal screw cap was punctured with an ice pick and utilizing the pick as a "needle valve," unpolymerized vinyl chloride was allowed to escape slowly without entrainment or frothing losses of the solution. The screw cap was then removed, the solution poured into 500 ml. of stirred 2B ethanol and the bottle and cap rinsed twice with 10-ml. portions of acetone. The polymer which precipitated as a fine powder was filtered on a Buchner funnel and washed with three fresh 500-ml. portions of denatured alcohol vigorously agitated in a Waring blender. The sample was finally filtered, dried in a circulating air oven at 50° for twenty-four hours and weighed. The product was analyzed in duplicate for chlorine by the Parr bomb method. Polymerization times, conversions and analytical data are summarized in Table I.

Emulsion.—A master emulsifier solution buffered to *p*H 8.0, comprising 500 g. of a 0.1 molar boric acid solution, 39.7 g. of 0.1 *N* sodium hydroxide, 10 g. of Santomerse D (the product of Monsanto Chemical Co.) and 8.3 g. of a 30% hydrogen peroxide solution was prepared. All emulsion polymerizations employed 100 ml. of this solution and 50 g. of total monomers. Appropriate amounts (Table I) of styrene and emulsifier solution weighed into 200-ml. pressure bottles were cooled in a Dry Ice-bath. A suitable volume of liquid vinyl chloride also cooled to Dry Ice temperatures was added. A metal cap with tinfoil liner was tightly screwed on the bottle which was allowed to warm to room temperature and weighed. Vinyl chloride added was determined by difference. The bottle was rotated end over end in a constant temperature water-bath regulated to 50 ± 0.05°. Polymerization times are shown in Table I. No convenient method was found for determining when low conversions had been attained, consequently many experiments were carried out to obtain the few results reported. On cooling to room temperature, the bottle was weighed. Weight losses during polymerization were 0–0.2 g. and, as explained above, a mean value was used for vinyl chloride monomer concentrations. The ice pick technique was used for venting vinyl chloride monomer, particular care being necessary in this case because of frothing. The screw cap was then removed and the emulsion poured into 500 ml. of 2B ethanol vigorously agitated in a Waring blender and the bottle and cap rinsed twice with 10-ml. portions of distilled water. The resulting suspension was heated to 60° and allowed to stand overnight to complete the coagulation. The product was filtered on a Buchner funnel, washed successively with three 1000-ml. portions of fresh alcohol, two 1000-ml. portions of distilled water, two 1000-ml. portions of alcohol, and then dried at 50° in a circulating air oven for twenty-four hours. Duplicate chlorine analyses by the Parr bomb method were obtained. Polymerization times, conversions and analytical data are summarized in Table I.

Vinyl Chloride–Methyl Acrylate Copolymerizations.—These copolymerizations were carried out in mass using 100-g. of total monomers. A polymerization technique identical with that described above for acetone solution polymerizations was employed. The water-bath temperature was regulated to 50 ± 0.05°. Vinyl chloride weight losses were 0–0.1 g. and a mean value was taken as before. After venting vinyl chloride monomer at room temperature, the products from the first four experiments (Table II) were precipitated by pouring the solution into 500 ml. of 2B ethanol vigorously agitated in a Waring blender. The resulting fine powder was filtered on a Buchner funnel, washed with three 1000-ml. portions of fresh alcohol and dried in a circulating air oven at 50° for forty-eight hours, then weighed. Products from the last four experiments were worked up in an identical way except that hexane was used instead of ethanol. In these cases a rubbery fibrous material was obtained instead of a fine powder. Since Parr bomb chlorine determinations gave erratic results for this copolymer series, chlorine analyses in duplicate were made by the Thompson–Oakdale method. Analytical data, conversions and polymerization times are summarized in Table II.

Vinyl Chloride–Acrylonitrile Copolymerizations.—This series was prepared in acetone solution using 50 g. of acetone and 50 g. of total monomers. The technique for charging the bottle and for polymerizing was identical to the method used for the vinyl chloride–styrene system in acetone solution. A water-bath temperature of 50 ± 0.05° was employed. Since the copolymers produced in this system were insoluble in the monomer–acetone solution, conversions were easily estimated from the amount of polymer formed. The bottles were cooled to room temperature, weighed and unpolymerized vinyl chloride released. Weight losses for this series were 0–0.4 g. and a mean value was taken as before. The fine suspension of copolymer was poured into 500 ml. of stirred 2B ethanol, filtered on a Buchner funnel and washed with three 1000-ml. portions of fresh alcohol. After drying at 60° for twenty-four hours in a circulating air oven, the product was weighed and analyzed in duplicate for chlorine by the Parr bomb method. Data for this copolymer series are summarized in Table III.

Tripolymer Experiments

Vinyl Chloride–Styrene–Methyl Acrylate.—These samples were prepared by mass polymerization in sealed

Pyrex tubes using 100 g. of total monomers. Appropriate amounts (Table IV) of styrene, methyl acrylate and benzoyl peroxide were weighed into a heavy-walled Pyrex tube 1" in diameter, 2' long and constricted 3" below the open end. The solution was cooled in a Dry Ice-bath and a suitable volume of cooled vinyl chloride was added. The tube was sealed, allowed to warm to room temperature and the amount of vinyl chloride added determined by weight difference. The tube was immersed vertically in a water-bath regulated to 50 ± 0.05°. When a slight increase in viscosity was observed the tube was removed, cooled to room temperature and weighed. No vinyl chloride was lost in either experiment. The tube was cooled in a Dry Ice-bath, the constricted end opened and the whole allowed slowly to warm to room temperature. The solution was then poured into 500 ml. of 2B ethanol vigorously agitated in a Waring blender. The resulting fine powder was filtered on a Buchner, washed with three fresh 1000-ml. portions of alcohol. After drying the product for twenty-four hours at 50° in a circulating air oven, it was weighed, analyzed in duplicate for chlorine by the Thompson-Oakdale method and for carbon and hydrogen by the micro method. Polymerization times, conversions and analytical data are summarized in Table IV.

Vinyl Chloride-Styrene-Acrylonitrile.—These samples were prepared by mass polymerization in screw-cap 200-ml. pressure bottles using 60 g. of total monomers. The bottle was charged by adding appropriate weights (Table IV) of styrene, acrylonitrile and benzoyl peroxide to the bottle, cooling and adding vinyl chloride as before. The bottle was rotated end over end in a constant temperature water-bath first at 50°, then at 25° for the times shown in Table IV. Weight losses were 0-0.2 g. for the experiments. After venting vinyl chloride, the slightly viscous solution was poured into 500 ml. of stirred 2B ethanol and the bottle and cap rinsed with two 10-ml. portions of benzene. The resulting fine powder was filtered on a Buchner funnel, washed with three 1000-ml. portions of fresh ethanol and dried in a circulating air oven at 60° for forty eight hours. The sample was weighed, analyzed in duplicate for chlorine by the Parr bomb method and for nitrogen by the Kjeldahl method. Data for these experiments are summarized in Table IV.

Summary

Monomer-polymer composition curves for the systems vinyl chloride-styrene, vinyl chloride-methyl acrylate and vinyl chloride-acrylonitrile have been determined. Coincidence of the solution and emulsion curves for the system styrene-vinyl chloride provides additional evidence for the oil phase mechanism of emulsion polymerization. Numerical values for monomer reactivity ratios for these systems are reported. Using these data an experimental investigation of the validity of the tripolymer equation was made. Good agreement was obtained between calculated compositions and compositions actually obtained.

DAYTON, OHIO RECEIVED JUNE 9, 1947

[CONTRIBUTION FROM SMITH, KLINE AND FRENCH LABORATORIES]

Analgesics. II. A New Synthesis of Aminophthalidylalkanes

BY GLENN E. ULLYOT, HERBERT W. TAYLOR, JR., AND NORMAN DAWSON

Recently we reported[1] the synthesis of a series of aminophthalidylalkanes, one of which, 1-amino-1-phthalidylpropane hydrochloride, showed considerable activity as an analgesic agent. The method of synthesis resulted chiefly in the lower melting racemic form, isomer B, but both racemic forms (isomers A and B) were isolated by careful fractional crystallization. Pharmacological tests indicated a difference in the toxicity and analgesic activity of these isomers, isomer A being more active and more toxic. For this reason, a need arose for a more convenient method of preparing sufficient amounts of isomer A for further pharmacological and clinical studies. This was accomplished according to Scheme I; only isomer A (VIII) was obtained.

In the synthesis previously reported, the asymmetry of the carbon atom next to the benzene ring was established first. The presence of this asymmetric center undoubtedly operated during the formation of the second asymmetric carbon center, so that there resulted unequal amounts of the two racemic forms of the nitro compound and, consequently, of the amine hydrochloride. In the synthesis reported here, our results may be accounted for by the reversal of the order of establishment of the asymmetric centers.

On attempting to proceed directly from *o*-carboxybutyrophenone without recourse to ester formation, it was found that ethyl nitrite failed to react with an ethereal solution of the ketone in the presence of anhydrous hydrogen chloride. This may have been because the keto acid existed chiefly as a lactol; in any event, the ester V was readily converted to VI.

Catalytic reduction of α-isonitrosoalkylphenyl ketones in the presence of three equivalents of anhydrous hydrogen chloride in absolute alcohol[2] has been shown to proceed first at the isonitroso group and then at the carbonyl group. Catalytic reduction of VI was readily effected; the course of the hydrogen uptake is shown in Fig. 1.

Unless the crude V was thoroughly washed with bicarbonate, considerable decomposition occurred during distillation and resulted in a material contaminated with propylidenephthalide (III). However, even after taking into consideration the amount of propylidenephthalide present in various batches of keto ester, treatment of this material with ethyl nitrite did not result in complete conversion into VI except in the case of ester no. 2

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[1] Ullyot, Stehle, Zirkle, Shriner and Wolf, *J. Org. Chem.*, **10**, 429 (1945).

[2] Hartung, THIS JOURNAL, **53**, 2248 (1931).