ried out essentially as described for N,N'-dibenzylethylenediamine.[6]

Reaction of Monoamines with Dihalides.—N,N'-Diethylhexamethylenediamine was prepared from ethylamine and hexamethylene dibromide: In a 3-liter, three-necked, round-bottomed flask equipped with a dropping funnel, mechanical stirrer and Dry Ice condenser was placed 1102 g. (24.5 moles) of ethylamine. Hexamethylene dibromide (122 g., 0.5 mole) was added dropwise over a period of one hour to the refluxing ethylamine. It was occasionally necessary to cool the flask with ice. After the reaction mixture had been stirred for an additional one and one-half hours, the excess ethylamine was distilled and recovered for use in a second run (830 g. of ethylamine and 92 g. of hexamethylene dibromide). To the combined product was added a concentrated aqueous solution of 125 g. of sodium hydroxide. The oil layer was dissolved in ether and dried with anhydrous sodium sulfate. The ether was evaporated and the N,N'-diethylhexamethylenediamine was distilled.

N,N'-Diallylhexamethylenediamine was prepared in the same manner except that the mole ratio of allylamine to dibromide was only five to one and the temperature of the reaction was 25-35°.

Summary

Fifteen N-substituted diamines (disecondary and secondary–primary) have been synthesized through (1) the catalytic hydrogenation of dialdimines or amine-aldimines or (2) the reaction of monoamines with dihalides. The first method was used in all but two cases.

BUFFALO, N. Y.

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[6] Mason, *Ber.*, **20**, 270 (1887).

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

Copolymerization. I. The Mechanism of Emulsion Copolymerization of Styrene and Acrylonitrile

BY REID G. FORDYCE AND EARL C. CHAPIN

The general theory of chain propagation processes in vinyl copolymerizations has been discussed by several investigators,[1-8] who have shown that the composition of copolymer molecules forming in a given system at any time is dependent primarily upon the monomer concentrations at that instant. Moreover, general equations describing the monomer–polymer composition relationship have been derived.[1,2,5] Experimental data determined for mass polymerizations have been reported[2,4,6,7] showing good agreement with the general equations and the numerical values of several propagation rate constant ratios have been elucidated. It appeared possible therefore that a comparison of the monomer–polymer composition curve obtained by emulsion polymerization with the curve obtained by mass polymerization might throw some light on the mechanism of emulsion polymerization.

For this work, styrene and acrylonitrile were selected as co-monomers, since Mayo, Lewis and Hulse[4] had already determined their propagation rate constant ratios for bulk polymerization. Copolymerizations were carried out in mass using an oil soluble catalyst and in emulsion using an oil soluble and a water soluble catalyst. The polymerizations were allowed to proceed to low conversions (mainly <4%) and the initial polymer was isolated and purified. The amount of combined acrylonitrile in the initial copolymer was determined by duplicate Kjeldahl analyses.

Results and Discussion

The results of the investigation are summarized in Table I from which the monomer–copolymer composition curves, Fig. 1, for the three series of experiments were drawn. In determining the monomer reactivity ratios for styrene and acrylonitrile, the differential form of the Mayo and

TABLE I

Monomer, mole % acrylonitrile	Time at polymerization temp., min.	Wt. % conversion	Nitrogen analyses, %		Copolymer, mole % acrylonitrile
			I	II	
(Mass polymerization at 75°, 0.05% Bz_2O_2)					
6.46	120	2	2.20	2.16	15.0
12.25[a]	120	2	3.46	3.44	22.8[a]
22.47	120	2	4.63	4.19	28.2
32.92	120	2	5.69	5.50	34.6
48.60[a]	120	2	6.94	6.86	41.0[a]
62.63	120	2	7.90	7.87	45.5
80.28[a]	...	2	9.85	9.83	53.8[a]
(Emulsion polymerization at 60°, 0.1% Bz_2O_2)					
9.36	124	0.7	2.20	2.20	15.1
17.90	...	0.7	3.54	3.41	22.9
32.92	130	4.9	5.51	5.50	34.0
45.68	66	2.6	6.34	6.10	37.7
66.25	338	3.4	7.54	7.44	43.7
(Emulsion polymerization at 75°, 0.2% $K_2S_2O_8$)					
8.24	195	3.1	1.99	1.86	13.4
14.86	28	8.5	3.27	3.15	21.4
18.83	25	3.2	3.69	3.69	24.2
24.93	20	1.9	4.37	4.34	28.0
36.32	10	6.6	5.60	5.58	34.5
45.69	20	3.0	6.39	6.38	38.5
66.25	...	3.6	7.72	7.48	44.2
94.64	...	1.7	12.77	12.65	64.6

[a] Data used for elucidating σ and μ.

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[1] Alfrey and Goldfinger, *J. Chem. Phys.*, **12**, 205, 322 (1944).

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

[3] Wall *ibid.*, **66**, 2050 (1944).

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

[5] Walling and Briggs, *ibid.*, **67**, 1774 (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).

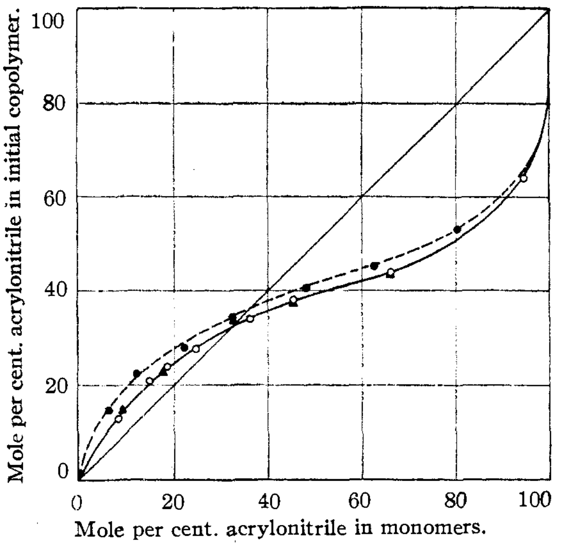

Fig. 1.—Monomer–polymer composition curves for styrene acrylonitrile: mass polymerization, ●-------; emulsion polymerization Bz_2O_2, ⊙————; emulsion polymerization, $K_2S_2O_8$, ▲————.

Lewis[9] equation was used since only products obtained at low conversions were analyzed. Using the data marked with an *a* in Table I and solving for σ and μ graphically according to the method of Mayo and Lewis,[2] the following monomer reactivity ratios were found

	Styrene	Acrylonitrile
Mass polymerization (Bz_2O_2 catalyst)	0.41 ± 0.08	0.03 ± 0.03

Mayo, Lewis and Hulse[4] reported values of 0.41 ± 0.08 and 0.04 ± 0.04 for this system.

From Fig. 1 it will be seen that monomer–polymer composition curves for the two series of emulsion experiments are identical within the error of analysis. It will also be observed that while the emulsion curves lie very close to the mass curve, the emulsion copolymers consistently contain slightly less combined acrylonitrile than the corresponding mass copolymer.

The values for the emulsion experiments were determined on the basis of monomer concentrations *charged to the reaction*, and it is reasonable to assume that most of the added monomers are present as the oil droplets of the dispersed phase. However, certain small amounts of styrene and acrylonitrile must be in true solution in the aqueous phase. The partition coefficients of styrene and acrylonitrile monomers between the two phases for this system are not known. However, the following solubility data give an insight into the trend which might be expected.

	100 g. water at 60.3°	100 g. aqueous 4% Santomerse D at 60.3°
Styrene	0.96 ± 0.05 g.	1.3 ± 0.3 g.
Acrylonitrile	11.0 ± 0.1 g.	12.8 ± 1.2 g.

From the solubility data, one would expect the relative concentration of acrylonitrile with respect to styrene to be lower in the oil droplet than the relative concentration of acrylonitrile to styrene charged to the reaction. Thus less combined acrylonitrile should be found in the emulsion copolymers than in the corresponding mass copolymers *if polymerization occurs in the oil phase.*

It is virtually impossible that relative monomer concentrations in the aqueous phase could be the same as the relative monomer concentrations added to the reactor for *all* the experiments reported. Unless aqueous phase concentrations equivalent to the charged monomers do exist, it is impossible to explain the proximity of the mass and emulsion curves on the basis of an aqueous phase mechanism of emulsion polymerization. It is therefore concluded that in the emulsion copolymerization of styrene and acrylonitrile the first copolymer molecules formed are propagated in a non-aqueous phase or at its interface but not to any appreciable extent in the aqueous phase.

Coincidence of the two emulsion curves also shows that an oil phase mechanism of emulsion polymerization is operative regardless of whether an oil soluble or a water soluble catalyst is employed.

The papers of W. V. Smith[10] on the theory of regulators in emulsion polymerization also report results consistent with an oil phase mechanism of emulsion polymerization.

If the oil phase mechanism of emulsion polymerization is valid generally, large deviations of the emulsion monomer–polymer composition curve from the mass curve would be predicted in cases where one of the co-monomers has a partition coefficient in favor of the aqueous phase. We are investigating a system of this type.

We are also investigating the validity of an oil phase mechanism for emulsion polymerizations carried to higher conversions.

Experimental

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

Acrylonitrile.—Redistilled American Cyanamid Co. material was used for all experiments.

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

Mass Polymerization.—Solutions comprising 50 g. of total monomers were prepared by adding appropriate weights of acrylonitrile, styrene and benzoyl peroxide to 2 oz. French square bottles. The concentrations employed are given in Table I. Air above the monomers was swept out with oxygen-free nitrogen and a metal cap screwed tightly on the bottle mouth. Copolymerizations were carried out in an air oven regulated to 75 ± 1°. After two hours, the slightly viscous solution was poured

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(9) $\frac{d[S]}{d[M]} = \frac{[S]}{[M]} \cdot \frac{\sigma[S] + [M]}{\mu[M] + [S]}$, where [S] and [M] refer to concentrations of unreacted monomers, d[S] and d[M] refer to the relative amounts of S and M in the copolymer molecules forming, σ and μ are the monomer reactivity ratios with respect to the two types of radicals involved.

(10) W. V. Smith, THIS JOURNAL, **68**, 2059, *et seq.* (1946).

into 1500 ml. of stirred denatured ethanol (2B) at room temperature. The polymer was obtained as a white precipitate and the mixture was boiled to complete the coagulation. On cooling, the clear supernatant alcohol solution was carefully decanted. Final purification was effected by similar treatment with two fresh 1500-cc. portions of denatured ethanol. After drying in an evaporating dish at 60° for forty-eight hours in a circulating air oven, the copolymer was analyzed in duplicate for nitrogen by the Kjeldahl method.

Emulsion Polymerization.—Potassium persulfate used was the product of the General Chemical Co. Santomerse D used was the product of Monsanto Chemical Co. (an alkyl aryl sodium sulfonate). A master batch of emulsifier solution was prepared by dissolving 200 g. of Santomerse D in 4800 ml. of distilled water. All emulsion polymerizations utilized 300 g. of this emulsifier solution and 150 g. of total comonomers. Emulsifier solution was added to a stirred 1-liter, three-necked flask and appropriate weights (Table I) of styrene, acrylonitrile and catalyst (benzoyl peroxide or potassium persulfate) were added. Catalyst concentrations are based on total monomers. The reaction mixture was stirred for one and one-half hours at room temperature and then, in the case of the benzoyl peroxide catalyzed experiments, raised to 60 ± 1° during twenty minutes by means of a Glas-Col mantle. The potassium persulfate catalyzed experiments were heated to 75 ± 2° over a thirty-minute period. Polymerization at these temperatures was continued until a low conversion had been obtained. Conversions during the reaction were approximated by estimating turbidity when 5 ml. of emulsion was added to 200 ml. of ethanol. Polymerization times at 60° and at 75° for the compositions employed are summarized in Table I. The entire reaction mixture was then poured into 3000 ml. of stirred ethanol and this mixture was boiled to coagulate the product. The polymer, which usually was obtained as a fine white powder, was filtered on a Buchner funnel, boiled with 1500 ml. of fresh ethanol and refiltered. This operation was then repeated. In some cases there was a tendency for polymer particles to stick together after the first boiling operation. Such products were re-comminuted by mixing in a Waring blender with fresh alcohol prior to filtration. The resulting fine powder was then purified by the above procedure. All products were dried in an evaporating dish at 60° in a circulating air oven for forty-eight hours. Conversions corrected for residue in the polymerization flask and for samples withdrawn during polymerization, were determined gravimetrically. These data and the nitrogen content of the products are given in Table I.

Solubility Determination.—Into four stoppered 50-ml. Erlenmeyer flasks were weighed two 25.000-g. portions of water and two 25.000-g. portions of 4% Santomerse D solution. The flasks were placed in a water-bath regulated to 60.3 ± 0.02°. Styrene and acrylonitrile were added dropwise to the water samples by means of a calibrated micro-pipet and the flasks agitated after each addition. Acrylonitrile was added two drops at a time and styrene was added a drop at a time. The saturation point was taken at the first appearance of turbidity and the amount of styrene and of acrylonitrile added was calculated from the number of drops added. A similar procedure was followed for the Santomerse D solutions and the turbidity was matched visually with that of the water solutions. Estimation of turbidity was more difficult in the case of the Santomerse solutions and, as shown above, the experimental error was larger.

Acknowledgments.—The authors are indebted to Miss M. Magin for the nitrogen determinations.

Summary

Proximity of the monomer–polymer composition curves for the system styrene–acrylonitrile determined for mass and emulsion methods of polymerization, is interpreted as giving support to an oil phase mechanism for emulsion polymerization.

Data are reported to show that an oil phase mechanism is operative in emulsion copolymerization for both oil soluble and water soluble catalysts.

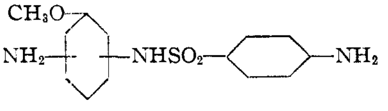
DAYTON, OHIO RECEIVED NOVEMBER 2, 1946

[CONTRIBUTION FROM THE DIVISION OF MEDICINAL CHEMISTRY, THE SQUIBB INSTITUTE FOR MEDICAL RESEARCH]

Aminosulfanilanisides[1]

BY FRANK H. BERGEIM, KATHYRN LOSEE AND W. A. LOTT

In our investigation of relatively simple carbocyclic compounds as possible antimalarials, we prepared several isomeric aminosulfanilanisides of the following general structure



Of the ten possible structural isomers using the three groupings shown above we have prepared the seven which are listed as the first seven compounds in Table I. In addition there are listed in Table I some related sulfanilamide end-products together with methods for their preparation and other pertinent data.

The penultimate intermediates required for the preparation of the end-products listed in Table I are listed in Table II. There is also included in this table an outline of the procedures used for the preparation of these intermediates. The outlined procedures are similar in many instances and are based on representative general procedures, A, B, C, D, E and F, illustrated by specific examples in the experimental part.

Many of the end-products in Table I were prepared by the acid hydrolysis of the corresponding acetylated intermediates of Table II. Other end-products of Table I were obtained by reducing the penultimate nitro intermediates of Table II with iron and hydrochloric acid, iron and acetic acid, or catalytically. The succinoyl and acetaldehyde bisulfite end-products required specific procedures which are described in the experimental part.

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[1] Presented before the Division of Medicinal Chemistry at the 109th Meeting of the American Chemical Society, Atlantic City, N. J., April 10, 1946