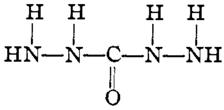
carbohydrazide is  $H\overset{H}{N}-\overset{H}{N}-\underset{O}{\underset{\|}{C}}-\overset{H}{N}-\overset{H}{N}H$, only one N-N bond has undergone hydrogenolysis. Thus it appears that a property of the carbohydrazide structure is this resistance to complete hydrogenolysis.

We have established the fact that carbohydrazide is a stronger acid than fluorene, while semicarbazide is weaker. That it is not much weaker follows from an observation of Conant and Wheland.[4] These investigators observed cases of several extremely weak acids in which salts of acids only slightly weaker reacted with them slowly while in cases in which the difference in acidity was great, the reaction was instantaneous. Since the appearance of the color of sodium fluoryl is delayed after an equivalent of sodium triphenylmethyl has been added to the hydrochloride of semicarbazide, it is concluded that semicarbazide is only slightly weaker as an acid than fluorene. By the same argument, urea is a much weaker acid than fluorene, since the yellow color of sodium fluoryl appears instantly when one drop of sodium triphenylmethyl is added to a solution of urea and fluorene. We may conclude that the relative acidity of these three compounds in liquid ammonia is: carbohydrazide > semicarbazide > urea. The NH_2 group is an electron attracting group, causing the semicarbazide nitrogen to become more acidic than that of urea through the inductive effect. The additional inductive effect of the second NH_2 group would cause carbohydrazide to be a slightly stronger acid than semicarbazide. We believe that the magnitude of the effect observed is much too great to be explained in this manner, however.

The difference in reducibility of the two substances parallels the acidity. The compound with the more positive N, carbohydrazide, should be the one which would add electrons more easily. Thus the stronger acid should be more readily reduced. This is the order actually observed.

One of the authors (J.D.R.) wishes to express his appreciation of a grant-in-aid from the Hynson, Westcott and Dunning Research Fund.

Summary

1. Carbohydrazide has been reduced to semicarbazide.

2. The relative acidity of carbohydrazide, semicarbazide and urea has been determined in liquid NH_3.

3. Fluorene and indene are suitable acid indicators in liquid NH_3.

4. Resistance to hydrogenolysis is a characteristic of semicarbazide structure.

BALTIMORE 18, MD. RECEIVED AUGUST 3, 1950

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

Copolymerization. VIII. Reactivity of Fumaronitrile in Vinyl Copolymerization

BY REID G. FORDYCE AND GEORGE E. HAM

In the course of an exploratory study of styrene copolymerization, mass copolymers of styrene and fumaronitrile were prepared. These copolymers, which were without exception incompatible, nevertheless showed a remarkable improvement over mass polystyrene with regard to heat distortion characteristics. It was realized that the incompatibility of these copolymers was probably the result of heterogeneity with respect to fumaronitrile content. Accordingly, an investigation of fumaronitrile reactivity in copolymerization with styrene was undertaken.

Results and Discussion

Various monomer mixtures of styrene and fumaronitrile dissolved in dioxane were allowed to polymerize to low conversions. Copolymerization was interrupted by precipitation of the slightly viscous copolymer solutions in ethanol, followed by thorough washing of the fibrous copolymer with more ethanol. The samples after drying were analyzed for nitrogen by the Kjeldahl method and the fumaronitrile content of the copolymers was calculated. As determined from the slope of the copolymerization curve (Fig. 1) at 0% fumaronitrile, the reactivity of fumaronitrile monomer for a styrene free radical is approximately 11.0 times as great as the reactivity of styrene for a styrene free radical. Since the completion of this research, Lewis and Mayo[1] have reported reactivity ratios for styrene and fumaronitrile. However, their calculated values ($r_1 = 0.19 \pm 0.03$, $r_2 = 0.0$) differ from those reported here. Monomer reactivity ratios for the system styrene–fumaronitrile were calculated by the Mayo and Lewis intersection method[2] and by curve fitting of experimental points, but no consistent values could be obtained. The reactivity of fumaronitrile unexpectedly diminishes at higher concentrations, causing deviation from the theoretical copolymerization curve. Accordingly, the initial slope was taken as the best indication of fumaronitrile reactivity, and yielded an r_1 value of 0.09 ± 0.005 and an r_2 value of 0.0. The anomalous behavior characteristic of the system styrene–fumaronitrile has also been observed with styrene–maleic anhydride.[3] In the case of styrene–fumaronitrile an azeotrope point of 38 mole % was obtained instead of the ~50 mole % obtained with styrene–maleic anhydride. No completely satisfactory explanation of the copolymerization behavior of styrene and fumaronitrile has been found. However, at higher fumaronitrile concentrations the opportunity for electrostatic repulsion between fumaronitrile monomer and polymer chains rich

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(1) F. M. Lewis and F. R. Mayo, THIS JOURNAL, **70**, 1533 (1948).

(2) F. R. Mayo and F. M. Lewis, *ibid.*, **66**, 1594 (1944).

(3) T. Alfrey, Jr., and E. Lavin, *ibid.*, **67**, 2044 (1945).

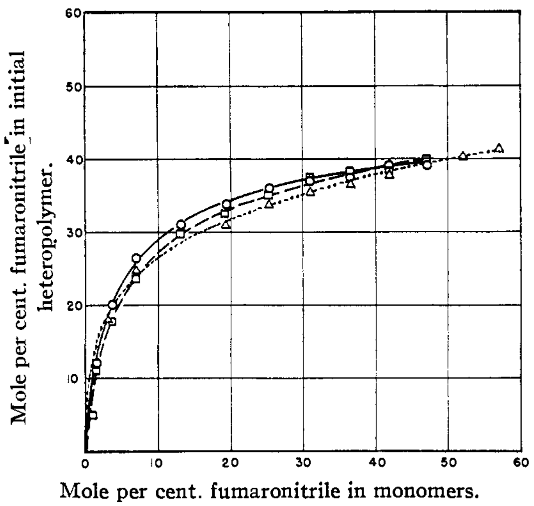

Fig. 1.—Monomer-polymer composition curves for the system styrene–fumaronitrile: mass polymerization, —O—; emulsion polymerization, —□—; solution polymerization —△—.

in fumaronitrile would exist and this phenomenon may explain the unusual copolymerization curve. The presence of two strong electron-withdrawing nitrile groups within such a small molecule accounts for the strong alternation tendency in this system and perhaps the unexpected damping of fumaronitrile reactivity at higher concentrations. The fact that the similar system styrene–acrylonitrile obeys the copolymerization equation well ($r_1 = 0.41 \pm 0.08$, $r_2 = 0.03 \pm 0.03$)[4] can be reconciled with these data on the basis of less electron asymmetry in the case of acrylonitrile than in the case of fumaronitrile. However, no comparative dipole measurements have been made. It is significant that the azeotrope composition in the system styrene–acrylonitrile is 36% acrylonitrile which is only 2% less than the azeotrope composition in the system styrene–fumaronitrile.

Since fumaronitrile possesses substituents on both carbons separated by a double bond it is not surprising that it shows no reactivity toward a chain ending in a fumaronitrile free radical. Moreover, fumaronitrile shows no tendency to polymerize alone in the presence of peroxide catalysts.

Since strong alternating tendencies were observed in the copolymerization systems, styrene–fumaronitrile and α-methylstyrene–acrylonitrile as well as addition of olefins which do not homopolymerize (fumaronitrile and α-methylstyrene) to growing free radicals, it was of interest to explore the system α-methylstyrene–fumaronitrile. A copolymerization curve similar to that of styrene–fumaronitrile was obtained with a slightly greater alternation tendency (Fig. 2). The copolymerization curve once again did not fit the Lewis–Mayo copolymerization equation because of reduced fumaronitrile reactivity at higher concentrations. The same theory which was used to explain this phenomenon in the styrene–fumaronitrile system appears applicable here. The form of this copolymerization curve was predicted with fair accuracy from those already known for styrene–fumaronitrile, styrene–acrylonitrile,[4] and α-methylstyrene–acrylonitrile.[5] The reactivity of acrylonitrile toward a styrene free radical is 2.44 times as great as the reactivity of styrene toward a styrene free radical and the reactivity of acrylonitrile toward an α-methylstyrene free radical is ten times as great as the reactivity of α-methylstyrene for an α-methylstyrene free radical. If these differences can be assumed to carry over to fumaronitrile copolymerizations, one would expect fumaronitrile to be approximately 45 times as reactive as α-methylstyrene toward an α-methylstyrene free radical (four times $1/r_1$ of the styrene–fumaronitrile system). Determination of the fumaronitrile reactivity ratio (r_1) from the initial slope of the copolymerization curve indicated that the predicted reactivity is approximately correct ($r_1 = 0.022 \pm 0.005$, $r_2 = 0.0$).

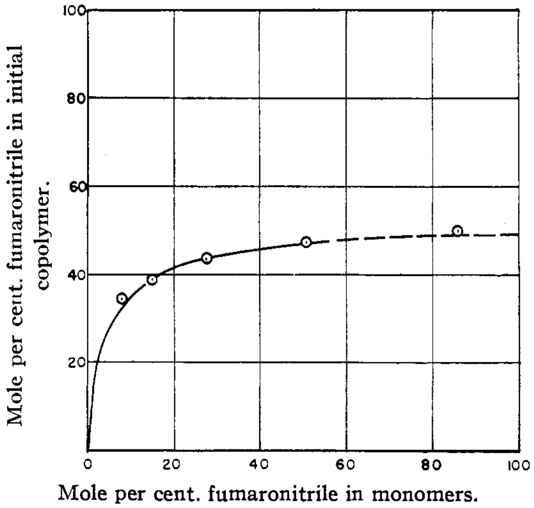

Fig. 2.—Monomer-polymer composition curve for the system α-methylstyrene–fumaronitrile solution polymerization.

An investigation of the heat distortion point (A.S.T.M.) of uniform copolymers of styrene and

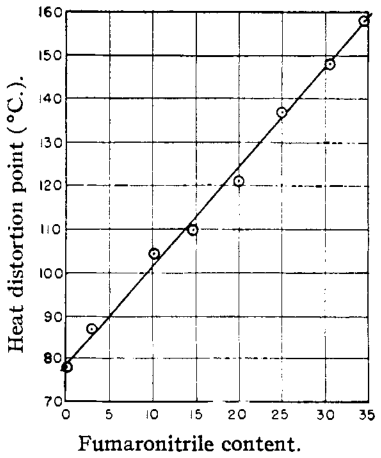

Fig. 3.—Heat distortion point (A. S. T. M.) of styrene–fumaronitrile copolymers as a function of fumaronitrile content.

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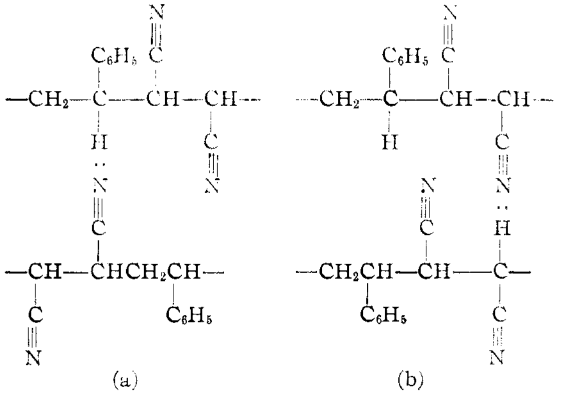
[4] R. G. Fordyce and E. C. Chapin, *ibid.*, **69**, 581 (1947).

[5] R. G. Fordyce, E. C. Chapin and G. E. Ham, *ibid.*, **70**, 2489 (1948).

fumaronitrile produced by interrupting mass copolymerizations at low conversions (<5%) indicated that the heat distortion point was directly proportional to the fumaronitrile content of the copolymer (Fig. 3).

Though it is not known definitely why fumaronitrile improves the thermal properties of styrene copolymers, it is believed that a likely explanation may be based on hydrogen bonding. Since the excellent thermal resistance of polyacrylonitrile is generally attributed to hydrogen bonding between nitrile groups and the hydrogens of adjacent chains which are α to nitrile groups, this is a reasonable assumption. There are two possible types of hydrogen bonding which may occur in styrene–fumaronitrile copolymers. The nitrile groups may bond with hydrogens activated by either nitrile groups or phenyl groups


(a) (b)

The fact that heat distortion point is directly proportional to fumaronitrile content supports the theory that the bonding is of type (a). If the bonding were of type (b), heat distortion point should vary as the square of fumaronitrile content.

It should be pointed out, however, that dipole interaction may contribute significantly to the improvement in heat distortion.

Copolymers of styrene and fumaronitrile containing over 10% fumaronitrile are soluble in acetone, whereas copolymers containing less fumaronitrile are not soluble. Similar solubility behavior has been noted in styrene–acrylonitrile, vinyl chloride–acrylonitrile, and vinylidene chloride–acrylonitrile copolymers in which all the homopolymers are insoluble in acetone. Apparently, nitrile groups, if properly spaced to decrease hydrogen bonding, lend solubility in ketone solvents to copolymers.

A summary of the experimental data on the copolymerization of styrene and fumaronitrile in mass, emulsion and dioxane solution is given in Table I and Fig. 1. Data on the copolymerization of α-methylstyrene and fumaronitrile are shown in Table II and Fig. 2. Figure 1 indicates the marked similarity among copolymerization curves of styrene and fumaronitrile obtained in mass, emulsion and dioxane solution. The lower fumaronitrile content of the emulsion copolymers may be explained on the basis of the solubility of fumaronitrile in water. However, the difference may not be significant since the solution curve is still lower. The similarity of these curves is taken as additional evidence of polymerization in a non-aqueous phase in emulsion. At this locus whether within micelle or swollen polymer particle the fumaronitrile content would be slightly reduced because of water solubility.

Experimental

Styrene monomer was the redistilled product of Monsanto Chemical Company.

α-Methylstyrene.—Redistilled Dow Chemical Co. product was used.

TABLE I

STYRENE–FUMARONITRILE

Monomer mole % fumaronitrile	Time at polymn. temp.		Wt. % conversion	Nitrogen, %		Heteropolymer mole % fumaronitrile
	Hr.	Min.		I	II	
Mass polymerization at 79°						
1.33	33	10	4.7	3.36	3.36	12.1
3.30	20	40	2.5	5.31	5.95	19.9
6.56	11	35	1.5	7.49	7.58	26.2
12.90	3	52	2.6	8.91	9.13	30.9
19.05	2	54	2.9	9.86	9.88	33.6
25.00	3	3	5.0	10.47	10.64	35.7
30.77	2	44	6.5	10.83	11.04	36.9
36.36	2	7	2.5	11.02	11.24	37.4
41.79	2	0	3.3	11.59	11.69	39.0
47.06	1	30	1.4	11.50	11.95	39.3
Emulsion polymerization at 60°						
0.66		338	6.1	1.36	1.50	5.2
1.33		175	1.5	3.06	3.10	11.1
3.30		123	0.5	4.21	4.43	15.4
6.56		84	3.6	6.61	6.74	23.4
12.90		42	2.9	8.47	8.60	29.4
19.05		23	2.9	9.42	9.49	32.3
25.00		20	3.6	10.10	10.53	35.0
30.77		10	3.9	10.79	11.19	37.0
36.36		15	3.2	11.12	11.35	37.8
41.79		7	3.5	11.39	11.60	38.6
47.16		20	2.7	11.80	11.97	39.7
Dioxane solution polymerization at 40°						
	Days					
1.33	5		4.4	3.42	3.43	12.3
2.66	5		5.5	5.08	5.13	18.1
6.56	5		5.8	6.99	7.04	24.5
19.05	4		8.3	8.93	9.01	30.8
25.00	4		7.6	9.63	10.07	33.5
30.77	3		4.5	10.34	10.45	35.2
36.36	3		5.0	10.73	10.83	36.4
41.79	3		3.9	11.24	11.25	37.8
47.16	3		2.4	...	11.88	39.7
52.15	3		3.7	11.88	12.04	40.0
57.14	3		2.1	12.33	12.42	41.2

TABLE II

α-METHYLSTYRENE–FUMARONITRILE

Monomer mole % fumaronitrile	Time at polymn. temp., hr.	Wt. % conversion	Nitrogen, %		Copolymer mole % fumaronitrile
			I	II	
Dioxane solution polymerization (50%) at 60°, 0.1% Bz_2O_2					
7.37	3	0.4	9.34	9.28	34.6
14.35	3	1.0	10.53	10.41	38.4
27.4	3	2.6	11.95	11.97	43.0
50.2	3	5.0	13.30	13.14	47.2
85.5	3	2.2	14.38	14.27	50.0

Fumaronitrile.—The purified product was obtained by the dehydration of fumaramide with phosphorus pentoxide.[6]

Santomerse D.—The product of Monsanto Chemical Co. was used.

Benzoyl Peroxide.—The Lucidol Corp. product was used as received.

Mass Copolymerizations.—A total of 100 g. of the styrene–fumaronitrile mixture was placed in a 4-oz. French square bottle. The concentrations of monomer used are given in Table I. Air above the monomers was displaced with nitrogen and a metal cap screwed tightly in place. Copolymerizations were carried out in an air oven regulated at 79 ± 1°. Polymerization was allowed to continue until a slight increase in viscosity was observed. The solution was then poured into 3000 ml. of stirred denatured ethanol (2B) at room temperature and the bottle was rinsed with ethanol. The mixture was boiled to complete coagulation and filtered. The copolymer was washed with two fresh 1500-ml. portions of ethanol. The copolymer was then dried in an evaporating dish for 24 hours at 60° in a circulating air oven. Duplicate micro-Dumas analyses were made on the copolymer samples. Analytical data and conversions are given in Table I.

Solution Copolymerizations.—Appropriate monomer mixtures (100 g.) with equal weights of dioxane were charged to 8 oz. French square bottles. These mixtures were allowed to polymerize and the copolymer was isolated in the same way as described for mass copolymerizations.

Emulsion Copolymerizations.—A master batch of emulsifier solution was prepared by dissolving 200 g. of Santomerse D in 1800 ml. of distilled water. All emulsion polymerizations utilized 300 g. of this emulsifier solution and 150 g. of total monomer. Emulsifier solution was added to a stirred 1-liter, three-necked, round-bottomed flask and appropriate weights of styrene and fumaronitrile were added. The reaction mixture was stirred for 1.5 hours at room temperature and then heated to 60° over a 30-minute period. Polymerization was continued until a low conversion was obtained. Conversions during reaction were approximated by estimating turbidity when 5 ml. of emulsion was added to 200 ml. of ethanol. 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 repeated. In some cases there was a tendency for polymer particles to stick together after the first boiling operation. Such products were recomminuted by mixing in a Waring Blendor with fresh alcohol prior to filtration. The resulting white powder was then purified by the above procedure. The copolymer was dried at 60° in a circulating air oven for 24 hours. Conversions corrected for residue in the polymerization flask and for samples withdrawn during the polymerization were determined gravimetrically.

Heat distortion points were determined by the A.S.T.M. method (ASTM D648-41T) employing an air-bath. Molded specimens (0.5″ × 0.5″ × 5.0″) were placed in the heat distortion apparatus and the temperature gradually raised from room temperature at the rate of 0.5° per minute until a deflection of 10 mils was obtained.

Summary

The monomer reactivity of styrene–fumaronitrile mixtures in mass, solution, and emulsion was determined. The similarity of monomer reactivity in the three systems is regarded as further proof of a non-aqueous locus of emulsion polymerization. The copolymerization of α-methylstyrene and fumaronitrile was studied and the predicted monomer reactivity ratios confirmed. A theory accounting for the direct proportionality of heat distortion point and fumaronitrile content of styrene copolymers is proposed.

DAYTON 7, OHIO RECEIVED JULY 12, 1950

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[6] deWolfe and van de Straete, *Bull. soc. chim. Belg.*, **44**, 288 (1935).

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF KANSAS]

The Effect of Fluorine Substitution on Medicinal Agents. III.[1] Synthesis of 2-Trifluoromethyl-1,4-naphthoquinone

BY ARTHUR F. HELIN,[2] AUGUST SVEINBJORNSSON[3] AND CALVIN A. VANDERWERF

The results obtained in the earlier studies in this series on the physiological and pharmacological properties of fluorine analogs of known medicinals have been of sufficient interest to warrant the extension of this program to include the fluorine derivatives of certain vitamins and compounds with vitamin-like activity. As a step toward this end, the synthesis of 2-trifluoromethyl-1,4-naphthoquinone, a trifluoro derivative of menadione of particular interest as a possible vitamin K antagonist,[4] has been carried out.

Experimental

2,5-Diacetamidobenzotrifluoride.—Exactly 19 g. (0.77 mole) of 2-nitro-5-acetamidobenzotrifluoride,[5] purified by recrystallization from benzene, dilute ethanol and dilute acetic acid, was dissolved in 50 ml. of acetic anhydride and shaken with hydrogen under a pressure of about 3 atmospheres in the presence of platinum oxide catalyst, while heat was applied by means of an infrared lamp. Absorption of hydrogen was complete in 2 hours. The cooled solution was filtered, diluted with 100 ml. of water and cooled in an ice-bath. Colorless crystals (14 g., 70%) of **2,5-diacetamidobenzotrifluoride**, m.p. 184–187°, separated slowly. After recrystallization from ethanol, the product melted at 188.4–189.1°.

Anal. Calcd. for $C_{11}H_{11}O_2N_2F_3$: N, 11.3. Found: N, 11.1.

Trifluoromethylbenzoquinone.—A 50-g. (0.19 mole) portion of 2,5-diacetamidobenzotrifluoride was heated with a solution of 255 ml. of concentrated sulfuric acid in 770 ml. of water until all of the solid had dissolved, indicating that hydrolysis was complete. The hot solution was decolorized by filtration with charcoal. It was placed in an ice-bath, 750 ml. of benzene was added and the resulting heterogeneous system was cooled to 8°. A solution of 68 g. (0.26 mole) of sodium dichromate dihydrate in 125 ml. of water was added with vigorous stirring at such a rate that the temperature did not rise above 10°. The mixture was stirred for 2 hours in the cold. The benzene layer was then

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[1] For the second paper in this series, see Lindenstruth, Fellman and VanderWerf, THIS JOURNAL, **72**, 1886 (1950). The authors are indebted to the Office of Naval Research for a grant which made this and continuing investigations possible.

[2] Government Laboratories, University of Akron, 351 West Wilbeth Road, Akron 1, Ohio.

[3] Electrochemicals Department, E. I. du Pont de Nemours and Company, Niagara Falls, New York.

[4] For a report on the effectiveness of monofluorophenylalanines and tyrosines as competitive inhibitors for their parent amino acids, see Mitchell and Niemann, THIS JOURNAL **69**, 1232 (1947).

[5] Obtained, along with small amounts of 2-nitro-3-acetamidobenzotrifluoride and of 2,3,4,6-tetranitro-5-acetamidobenzotrifluoride, m.p. 191.2–192.2°, by nitration of 3-acetamidobenzotrifluoride with fuming nitric acid (sp. gr. 1.5) in concd. sulfuric acid. The 3-acetamidobenzotrifluoride was prepared by nitration of benzotrifluoride, followed by catalytic reduction of the 3-nitro compound and acetylation of the resulting amine.