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Reductive Amination of Ethylene/Carbon Monoxide Polyketones. A New Class of Polyamines

BY D. D. COFFMAN, H. H. HOEHN AND J. T. MAYNARD

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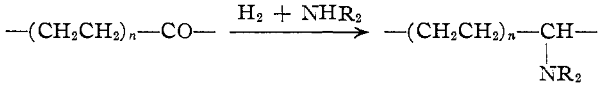
A new family of polyamines has been synthesized by reductive amination of the polyketones which result from copolymerization of ethylene and carbon monoxide. The polyamines have essentially the structure of a long-chain hydrocarbon with lateral primary, secondary or tertiary amine groups. They range in physical form from liquids to microcrystalline waxes. The structure has been confirmed both by infrared spectra and by the formation of typical amine derivatives such as salts, amides, N-oxides and ureas.

Introduction

Earlier studies in this Laboratory have made available, by the copolymerization of ethylene and carbon monoxide, a family of polyketones[1] which correspond in structure to a chain of recurring $-CO-$ and $-CH_2CH_2-$ units and which range from liquids to solid, high molecular weight polymers. A study of the chemistry of these novel polyketones has now shown that they can be converted to the corresponding polyamines. The present paper concerns the synthesis and characterization of this new class of polyamines.

Reductive amination of the ethylene/carbon monoxide polyketones has resulted in a new family of polyamines varying widely in molecular weight and physical form.



$$—(CH_2CH_2)_n—CO— \xrightarrow{H_2 + NHR_2} —(CH_2CH_2)_n—\underset{\displaystyle NR_2}{\underset{|}{CH}}—$$

The polyamines, therefore, consist of a hydrocarbon chain having amine groups as lateral substituents attached directly to the carbon atoms of the chain and distributed, on the average, at regular intervals predetermined by the carbon monoxide content of the parent polyketone. Since reductive amination of the carbonyl groups in the polyketones can be accomplished employing ammonia or various primary or secondary amines, polyamines can be prepared which possess a wide range of chemical reactivity.

The polyamines range in physical form from amber liquids to colorless, firm waxes, depending on their molecular weight and amine content. The polyamines form such derivatives as salts, amides and N-oxides. The polyamine salts, quaternary derivatives and N-oxides show surface-active properties, while less reactive derivatives such as the amides have characteristics similar to some of the natural waxes.

Polyamine Synthesis

The polyamines are prepared batch-wise by hydrogenation of a polyketone admixed with ammonia or an amine and any one of a variety of typical hydrogenation catalysts, employing super-atmospheric pressures and temperatures in the range 150–300°. When ammonia is used the products are polyprimary amines, while if primary or secondary amines are employed, the products are polysecondary or polytertiary amines, respectively. The most important variable in effecting reductive amination of the polyketones to obtain tractable polyprimary amines is reaction temperature. This must be sufficiently high to assure cleavage of any interchain secondary amine groups introduced by competitive reactions. Temperature requirements and other synthesis variables are discussed in following paragraphs.

Polyprimary Amines.—These have been prepared from ethylene/carbon monoxide copolymers ranging in carbon monoxide content from 40% to *ca.* 3% and in molecular weight from 450 to about 4000. The polyprimary amines obtained varied in neutral equivalent from 175 to $>$1000. The reductive amination was carried out in a steel pressure reactor with a several-fold excess of ammonia to repress secondary amine formation.

Polysecondary Amines.—Substitution of a primary amine for ammonia in the reductive amination yielded polysecondary amines. Such polyamines have been prepared by use of methylamine, ethylamine, ethanolamine and octadecylamine. The use of ethylenediamine led to cross-linked, rubbery polymers.

Polytertiary Amines.—When secondary amines were employed in the reductive amination, the products were polytertiary amines. Dimethylamine, diethylamine, pyrrolidine and morpholine have been used.

Catalysts.—Almost every typical hydrogenation catalyst tested including Raney nickel, supported nickel, reduced cobalt oxide, copper chromite and noble metal catalysts, has been effective in the reductive amination. The results of reductive aminations by means of four representative catalyst preparations are shown in Table I. A 25% nickel-on-kieselguhr catalyst has been commonly employed, usually at 5–10% concentration based on polyketone. Catalyst concentration is not critical, although concentrations of less than 2–4% of the commonly used nickel-on-kieselguhr catalyst were in some cases inadequate for amination, as shown in Table II. The use of noble metal catalysts, *e.g.*, 1 to 2% of a 10% palladium-on-charcoal, alone or in combination with the nickel catalyst, has often given polyamines of lighter color than could be obtained with nickel alone. The use of excessive amounts of the noble metal catalysts in some cases has caused a high degree of deamination of the products to waxy hydrocarbons, presumably by hydrogenolysis of the C–N bonds. For example, a polyketone of 11.4% carbon monoxide gave a polyamine of neutral equivalent 468 with 85 mole

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(1) M. M. Brubaker, D. D. Coffman and H. H. Hoehn, THIS JOURNAL, **74**, 1509 (1952).

% recovery of carbonyl and amine groups in the product when aminated with nickel-on-kieselguhr catalyst by procedure II (see Experimental). The same polyketone yielded a polyamine of neutral equivalent >1000 with only 34 mole % recovery of carbonyl and amine groups when a 5% ruthenium-on-alumina catalyst was employed. The latter product was essentially an inert wax, barely dispersible in dilute acetic acid, while the nickel product was a typical acid-soluble polyamine.

TABLE I

EFFECT OF NATURE OF CATALYST ON THE REDUCTIVE AMINATION OF AN ETHYLENE/CARBON MONOXIDE POLYKETONE

Polyketone: 16.1% carbon monoxide, 1790 mol. wt.

Catalyst	Catalyst concn.,[b] %	Composition of polyamine[a]: Nitrogen, %: Total	Nitrogen, %: Primary	Nitrogen, %: Primary/total	Carbonyl, %	Neut. equiv.
25% Nickel-on-kieselguhr	8	5.71	4.46	0.78	1.52	286
25% Nickel-on-kieselguhr +	6					
10% Palladium-on-charcoal	2	5.36	3.93	.73	4.29	280
Reduced cobalt oxide	10	4.98	3.17	.64	2.92	358
Barium–copper[c] chromite	20	4.96	3.61	.73	3.62	338

[a] Prepared according to procedure I (see Experimental). [b] Based on polyketone. [c] *Cf.* "Reactions of Hydrogen," by H. Adkins. Univ. of Wisconsin Press, Madison, Wis., 1937, p. 12.

TABLE II

EFFECT OF CATALYST CONCENTRATION ON THE REDUCTIVE AMINATION OF AN ETHYLENE/CARBON MONOXIDE POLYKETONE

Polyketone: 15.2% carbon monoxide, 1750 mol. wt.

Catalyst concn., % (on polyketone)	Composition of polyamine[a]: Nitrogen, %: Total	Nitrogen, %: Primary	Nitrogen, %: Primary/Total	Carbonyl, %	Neut. equiv.	Form
1	4.33	1.04	0.24	7.50	523	Insol. gel
4	4.96	2.98	.60	2.66	320	Soft wax
25	4.90	3.24	.66	2.43	304	Soft wax

[a] Prepared according to procedure I (see Experimental).

Temperature.—The use of a sufficiently high temperature is probably the most important factor in the formation of polyprimary amines. The minimum satisfactory temperature depends on the molecular weight and composition of the polyketones being aminated, but generally 150 to 200° is necessary. Low molecular weight polyketones have been aminated at temperatures as low as 100°, while polyketones known by their rheological behavior to be cross-linked have required a temperature of 250° to yield tractable polyamines. The relationship of temperature to degree of amination is illustrated in Tables III, IV and V. Comparison of the data of these tables shows that (1) short reaction times and low temperatures tend to give gelled, incompletely aminated products apparently cross-linked by interchain secondary amine groups, (2) polyketones of lower carbonyl content give products with a higher proportion of primary amino nitrogen, since the predominating 1,4-dicarbonyl structures in polyketones of high carbonyl content tend to form cyclic pyrrolidine units and (3) molecular weight degradation becomes pronounced at higher temperatures, with some further loss in primary amine content due to hydrogenolysis of amine groups and perhaps some further cyclization.

TABLE III

EFFECT OF TEMPERATURE ON REDUCTIVE AMINATION OF HIGH CARBON MONOXIDE CONTENT POLYKETONE

Polyketone: 31.2% carbon monoxide, 7250 mol. wt.

Temp., °C.	Composition of polyamine[a]: Nitrogen, %: Total	Nitrogen, %: Primary	Nitrogen, %: Primary/Total	Carbonyl, %	Neut. equiv.
175	[b]	[b]	[b]	[b]	[b]
200	9.13	5.00	0.55	4.97	236
225	9.12	4.52	.50	3.99	211
250	8.52	4.85	.57	3.85	206
275	8.29	3.47	.42	4.15	178
300	8.08	2.97	.37	4.10	180

[a] Prepared by procedure II (see Experimental). [b] Product gelled.

TABLE IV

EFFECT OF TEMPERATURE ON REDUCTIVE AMINATION OF LOWER CARBON MONOXIDE CONTENT POLYKETONE

Polyketone: 11.6% carbon monoxide, 1500 mol. wt.

Temp., °C.	Composition of polyamine[a]: Nitrogen, %: Total	Nitrogen, %: Primary	Nitrogen, %: Primary/Total	Carbonyl, %	Neut. equiv.
150	[b]	[b]	[b]	[b]	[b]
200	4.31	3.67	0.85	2.60	407
230	4.30	3.52	.82	3.04	364
260	4.26	3.20	.75	1.07	363
300	4.09	2.89	.71	2.12	362

[a] Prepared by procedure I (see Experimental). [b] Insoluble gel.

TABLE V

EFFECT OF VARIATIONS IN AMINATION CONDITIONS ON COMPOSITION AND MOLECULAR WEIGHT OF POLYAMINE

Polyketone: 10.3% carbon monoxide, 2905 mol. wt.

Temp., °C.	Pressure, atm.	Time, hr.	Composition of polyamine[a]: Nitrogen, %: Total	Nitrogen, %: Primary	Nitrogen, %: Primary/Total	Carbonyl, %	Neut. equiv.	Mol. wt.
150	300	10.0	[b]	[b]	[b]	[b]	[b]	[b]
250	600	0.5	2.58	2.08	0.81	5.04	713	3045
250	600	2.0	3.10	2.10	.68	1.00	699	2905
250	600	10.0	2.72	2.15	.79	1.68	650	2665
300	500	10.0	2.46	1.76	.72	1.12	694	1910

[a] Prepared by procedure I (see Experimental). [b] Insoluble gel.

Pressure.—The pressures required for amination depend on the attainment of a reasonable partial pressure of hydrogen in addition to the pressure developed by the ammonia present. The autogenous ammonia pressure may amount to several hundred atmospheres at the temperatures used. Most preparations during this study have been made at *ca.* 600 atm. pressure. By the use of reactors of high capacity and relatively small charges it has been possible, however, to carry out aminations at pressures as low as 150 atm. Variations in amination pressure over the minimum requirements do not materially affect the results obtained, as shown in Table VI.

TABLE VI

EFFECT OF PRESSURE ON REDUCTIVE AMINATION OF AN ETHYLENE/CARBON MONOXIDE POLYKETONE

Polyketone: 11.2% carbon monoxide, 2275 mol. wt.

Pressure, atm.	Composition of polyamine[a] Nitrogen, % Total	Primary	Primary/Total	Carbonyl, %	Neut. equiv.	Mol. wt.
150	3.70	2.69	0.73	1.56	422	1815
300	3.75	2.49	.66	2.50	412	2140
600	3.76	2.71	.67	1.79	421	2290

[a] Prepared by procedure I (see Experimental).

Reaction Time.—As a matter of convenience most runs have been allowed to continue for 10 to 15 hours, although it has appeared that conversion is essentially complete within one hour. Under the conditions employed and in the equipment used, consumption of hydrogen has been so small that the course of the reaction could not be followed by change in gage pressure. A series of aminations carried out for varying periods is summarized in Table VII. It can be seen that no significant changes in the products can be related to variations in reaction time.

TABLE VII

EFFECT OF TIME OF REDUCTIVE AMINATION ON POLYAMINES FROM AN ETHYLENE/CARBON MONOXIDE POLYKETONE

Polyketone: 14.7% carbon monoxide, 2170 mol. wt.

Time, hr.	Composition of polyamine[a] Nitrogen, % Total	Primary	Primary/Total	Carbonyl, %	Neut. equiv.
0.5	5.39	3.84	0.71	1.38	299
1	5.58	3.66	.66	0.95	296
2	5.29	3.63	.69	1.43	294
5	5.28	3.27	.62	0.51	300
10	5.40	3.24	.60	0.81	286

[a] Prepared by procedure I (see Experimental).

Medium.—In most aminations solvents have not been employed, although on occasion pure grades of benzene, toluene, xylene, cyclohexane, isopropyl alcohol and "Decalin" decahydronaphthalene have been used to reduce the viscosity of the reaction mixture. The degree of amination was not affected by these solvents except in certain cases in which the use of benzene in an amount four to ten times the weight of polyketone used apparently resulted in some inhibition of the reductive amination. Thiophene-containing benzene definitely inhibited the reaction.

Characterization of the Polyamines

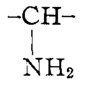
Physical Properties.—The polyamines are viscous liquids, soft, tacky gums or firm, microcrystalline waxes depending upon their molecular weight and amine content. The wax-like polyamines are generally of higher molecular weight and lower amine content. Polyamines of neutral equivalent 600–700 or less are readily soluble in 5% acetic acid, while those of higher neutral equivalent (*i.e.*, lesser amine content) are usually insoluble but dispersible in acid. The polyamines are soluble in very dilute mineral acids, for instance 1% hydrochloric acid, but are insoluble in more concentrated monobasic mineral acids and in polybasic acids such as sulfuric and phosphoric acids. The polyamines are soluble in aromatic hydrocarbons, chloroform and carbon tetrachloride. They are only moderately soluble in cyclohexane, isopropyl alcohol and dioxane and are very slightly soluble in ketones and the lower alcohols.

Nitrogen Content.—The neutral equivalent of the polyamines has been determined by perchloric acid titration in glacial acetic acid solvent, total nitrogen by the Dumas procedure, and primary amino nitrogen by the conventional Van Slyke procedure. As a rule, primary amino nitrogen content has been found to be less than total nitrogen. This has been attributed largely to the introduction of secondary amino groups through amination of unreacted carbonyl groups by previously formed primary amino groups to yield interchain cross-links, and/or through cyclization of 1,4-diketone moieties by reductive amination to introduce pyrrolidine rings. The latter effect is particularly pronounced in polyamines prepared from polyketones having low ethylene/carbon monoxide ratios and hence a high proportion of 1,4-diketone structures. In general, the sum of the mole per cent. nitrogen plus unconverted carbonyl content of the polyamines is appreciably less than that expected on the basis of the carbon monoxide content of the parent polyketone, and this difference is accounted for by the mechanisms suggested. This is sometimes not the case for polyamines deliberately made under insufficiently vigorous reaction conditions, as in the first example of Table II.

Table VIII summarizes the composition and properties of a series of polyprimary amines made from polyketones of molecular weights ranging from 1000–2500 and of carbon monoxide content ranging from 40 to 3.2%, these percentages corresponding to ethylene/carbon monoxide mole ratios of 1.5/1 to 30/1. It can be seen that the polyamine from a polyketone comprising 40% carbon monoxide contains a predominance of non-primary amino nitrogen, while those from polyketones of low carbon monoxide content contain largely primary amino nitrogen. The neutral equivalents are generally somewhat higher than would be expected on the basis of nitrogen content.[2] Polyamines of higher amine content are generally softer in consistency and are more highly colored.

The deficiency of the nitrogen plus residual carbonyl content of the polyamines from that expected from the carbon monoxide content of the parent polyketones can be seen from the data of Table VIII. The contribution of secondary amine and pyrrolidine ring formation to this effect is confirmed by infrared data (see next section), and some hydrogenolysis of primary amino groups may also be a contributing factor. The small proportion of unconverted carbonyl groups in the products is shown both by elementary analysis and by infrared absorption spectra.

Infrared Absorption Spectra.—Infrared spectra of the polyprimary amines support a structure comprised mainly of $-CH_2CH_2-$ and $\underset{\displaystyle NH_2}{\underset{|}{-CH-}}$ units.



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[2] The referee has kindly suggested that this effect might be a result of the tendency of the positively charged, partially neutralized polyelectrolyte to repel protons. See, for example, R. M. Fuoss and U. P. Strauss, *J. Polymer Sci.*, **3**, 246 (1948).

TABLE VIII

POLYPRIMARY AMINES FROM REDUCTIVE AMINATION OF ETHYLENE/CARBON MONOXIDE POLYKETONES IN AMMONIA[a]

Polyketone		Composition of polyamine						
Carbon[b] monoxide, %	Mol. wt.	Nitrogen, % Total	Primary	Primary/Total	Carbonyl, %	Neut. equiv.	Color	Form
40.0	1990	8.78	3.37	0.38	0.54	190	Amber	Liquid
21.8	2500	6.03	3.82	.63	2.03	255	Straw	Viscous liq.
18.5	1550	5.37	3.53	.66	2.01	270	Colorless	Soft grease
15.6	1790	4.25	3.30	.78	4.02	336	Colorless	Soft grease
11.4	1520	3.70	2.17	.59	2.61	420	Colorless	Soft wax
8.4	1650	2.76	1.68	.61	0.32	585	Colorless	Firm wax
7.2	1450	2.17	1.41	.65	0.58	643	Colorless	Firm wax
6.4	1030	2.20	1.88	.85	2.73	905	Colorless	Soft wax
4.4	1020	1.22	1.39	(1.00)	0.00	1510	Colorless	Hard wax
3.2	1450	1.21	1.06	.88	1.22	>1000	Colorless	Soft wax

[a] Prepared by procedure I (see Experimental). [b] Note that weight % carbon monoxide is equivalent to mole % carbonyl content.

A typical polyamine, prepared according to procedure I (see Experimental) from a polyketone of 20.0% carbon monoxide content and 4900 molecular weight, with isopropyl alcohol solvent, was a soft wax containing 6.00% total nitrogen, 3.30% primary amino nitrogen and 4.93% unreacted carbonyl groups. It had a neutral equivalent of 263 and a molecular weight of 1650. The presence of primary amino groups was confirmed by characteristic infrared absorption bands at 6.1 and 12.4 μ. A band attributed to the –NH– groups also was found, at 3.0 μ. The other absorption bands bore a close relationship to those shown by the parent polyketone. A weak band was observed at 5.86 μ due to carbonyl groups that did not react. Bands arising from the ethylene component of the polyketone are also present in polyamine spectra, for example absorption at 3.4 and 13.9 μ which is assigned to carbon–hydrogen structures. The nature of the absorption at 13.9 μ varies with the composition of the polyketone employed for reductive amination. Polyketones which have nearly one carbonyl for each ethylene unit show a weak singlet band at 13.9 μ.[1] As the proportion of ethylene is increased, the intensity of the absorption in this region increases and the band becomes a doublet. Doublet character is associated with structures having four or more methylene units in a chain. Thus, polyamines prepared from polyketones of high carbon monoxide content show a weak, singlet absorption at 13.9 μ, while polyamines from polyketones of lower carbon monoxide content show a more intense band of the doublet type.

Reaction Mechanisms.—Consideration of the composition and properties of this new class of polyamines leads to the conclusion that the apparently simple conversion of a carbonyl group to a primary amine group is accompanied by side reactions when a multiplicity of carbonyl functions may be involved. The reductive amination of simple carbonyl compounds with ammonia invariably leads to some secondary and tertiary amine formation, apparently due to the amination of unreacted carbonyls by amino compounds formed early in the reaction.[3] In the case of the ethylene–carbon monoxide polyketones, amination under insufficiently vigorous conditions or in the presence of catalyst poisons yielded gelled, insoluble products. This result suggests strongly that secondary and tertiary amino groups are formed which act as cross-links between the chains. The presence of amine groups in the gelled amination products is indicated by partial solubility in dilute acetic acid. If the gelled polyamines are again subjected to amination conditions at higher temperatures, soluble polyamines are formed. It has been assumed that hydrogenolysis of secondary amine cross-links is involved in this change.

Derivatives of the Polyamines

Ethylene/carbon monoxide polyamines have been converted to several classes of derivatives, which are discussed briefly in the following paragraphs. Neutralization equivalent has been taken as a more reliable measure of reactivity of the polyamines than nitrogen content, and stoichiometry involved in the derivative preparations has in all cases been calculated on this basis.

Reaction with Formaldehyde.—The polyamines are insolubilized by the action of formaldehyde. Solutions in dilute acetic acid containing a few per cent. formaldehyde are stable, but if such a solution is allowed to dry the product is an insoluble resin.

Polyamine Salts.—Salts of the polyamines with formic, acetic, glycolic and lactic acids are water-soluble. In general, salts of higher molecular weight organic acids, of mineral acids and of polybasic acids are difficultly soluble in water and in organic solvents. Dilute solutions of polyamine hydrochlorides can be prepared, but concentrations of hydrochloric acid in excess of 1–2% cause precipitation of the polyamine hydrochloride. Various polyamine salts have been isolated by addition of the appropriate acid to a benzene solution of the polyamine followed by evaporation of the solvent. These salts are generally waxy to resinous solids. The polyamines react rapidly with carbon dioxide in benzene solution or in the form of thin films forming rubbery carbonates that are insoluble in organic solvents and water but are soluble in dilute acids or hot benzene with loss of carbon dioxide. These polyamine carbonates contain only about 25% of the theoretical amount of carbon dioxide. The addition of aqueous solutions of salts of long-chain acids such as sodium dodecyl sulfate or sodium car-

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(3) W. S. Emerson, "Organic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1948, Vol. IV, Chapter 3.

boxymethyl cellulose to aqueous polyamine acetate solutions results in immediate precipitation of the corresponding polyamine salts.

Quaternary Salts.—Tertiary polyamines have been converted to polyquaternary salts by the action of alkyl esters such as methyl iodide, benzyl chloride, octadecyl bromide and methyl cyclohexanesulfonate. Salt formation was carried out in benzene solution, and the products either precipitated from solution as resinous solids or were isolated by evaporation of the solvent. The polyquaternary salts were generally water-soluble.

Polyamine Oxides.—Water-soluble or dispersible polyamine oxides were formed when the polytertiary amines were treated with hydrogen peroxide in aqueous isopropyl alcohol or in aqueous dispersion. Evaporation of the solvents on the steam-bath gave gummy or resinous solids which oxidized potassium iodide and had neutral equivalents of the same order as the parent polytertiary amines.

Polymeric Amides.—Polyacetamides, stearamides, terephthalamides, phthalamic acids and cresotinyl amides have been made by appropriate procedures, *e.g.*, heating polyprimary amines with the carboxylic acids or acid anhydrides or by typical Schotten–Baumann reactions of acid chlorides with the polyamines in the presence of potassium carbonate. The polyamides were resinous waxes which had neutral, acidic or basic properties depending on whether an equivalent amount of acid, an equimolar amount of dibasic acid or a deficiency of monobasic acid was used.

Polyureas and Thioureas.—The addition of potassium cyanate or potassium thiocyanate to aqueous solutions of polyamine acetates caused rapid precipitation of the corresponding polyurea or polythiourea. These were resinous gums, insoluble in hydrocarbon solvents and water but soluble in isopropyl alcohol. Alcoholic solutions of the polyureas formed factice-like precipitates on addition of formaldehyde.

Experimental

Synthesis of Polyamines[4]

Polyprimary Amines. Procedure I.—The synthesis of a typical polyprimary amine is illustrated by the following experiment. A 400-ml. stainless steel-lined steel reactor, capable of withstanding pressures of 1000 atm., was swept with a stream of nitrogen. Into the reactor were introduced 50 g. of a polyketone of 10% carbon monoxide content and 2300 molecular weight, and 5 g. of a 25% nickel-on-kieselguhr catalyst. The reactor was then closed, cooled in a bath of Dry Ice–acetone, evacuated and 20 g. of anhydrous ammonia was distilled in through a flexible copper tube directly from a small ammonia cylinder. The reactor was placed in a mechanical shaker, connected to a high pressure source of hydrogen and cold pressured to about 200 atm. Agitation was started, and the temperature was brought to 200°, after which the pressure was adjusted to *ca.* 600 atm. These conditions were maintained for 15 hours. After the reactor had been allowed to cool, excess ammonia and hydrogen were carefully vented, the tube was opened, and the contents were diluted with thiophene-free benzene. The resulting mixture was transferred to a beaker and was heated to the boiling point to dissolve the product. The solution was filtered from catalyst through a büchner funnel in which a pad of diatomaceous earth about one-half inch thick had been formed. The filter was washed with fresh, hot thiophene-free benzene, and the combined filtrates were concentrated under a vacuum to remove solvent. The distillation flask was heated in an oil-bath to a final temperature of 100–125° under a pressure of about 1 mm., and the molten polyamine was purged with a stream of nitrogen for about one hour to ensure removal of all solvent. On cooling, there was obtained a colorless, firm wax, readily soluble in 5% acetic acid.

Anal. C, 81.72; H, 12.83; N, 3.86; O (by difference), 0.59; primary amino N, 2.73; neut. equiv., 416.

The synthesis of polyamines from polyketones of varying carbon monoxide content, molecular weight and solubility characteristics required variations in temperature and pressure and the use of a solvent medium in some cases. However, the great majority of runs followed the general pattern of procedure I. Procedures II through IV illustrate particular variations, such as the use of a solvent, amination at lower pressures by employing a smaller charge, and the preparation of larger batches of polyamines.

Procedure II.—A polyketone of 13.3% carbon monoxide content and 660 molecular weight was aminated as in procedure I except that 100 ml. of isopropyl alcohol was introduced as solvent. The product was a straw-colored, viscous liquid of neutral equivalent 368.

Procedure III.—Forty grams of a polyketone of 11.2% carbon monoxide content and 2275 molecular weight was aminated with 10 g. of ammonia in the presence of 4 g. of nickel-on-kieselguhr catalyst and 1 g. of 10% palladium-on-charcoal catalyst at 250° and 150 atm. pressure. The product was a colorless wax of neutral equivalent 422.

Procedure IV.—Larger-scale preparations were made in a 1400-ml. stainless steel rocker bomb. This reactor was charged in the same fashion as the smaller reactors. In a typical experiment 350 g. of polyketone of 8.1% carbon monoxide content and 3400 molecular weight, 200 g. of ammonia, 25 g. of nickel-on-kieselguhr and 5 g. of palladium-on-charcoal catalysts were hydrogenated for ten hours at 250° and 600 atm. The product was a colorless, firm wax of neutral equivalent 585.

Secondary Polyamines.—Synthesis conditions were identical with those for the primary analogs except that amines such as methylamine, ethylamine, etc., were substituted for ammonia. A typical preparation employed a charge of 50 g. of polyketone of 10.3% carbon monoxide content and 2000 molecular weight, 5 g. of nickel-on-kieselguhr catalyst and 100 g. of methylamine. The amination was carried out at 200° and 600 atm. pressure. The product was a hard, colorless wax, readily soluble in 5% acetic acid.

Anal. C, 81.91; H, 13.46; N, 3.66; O (difference), 1.97; neut. equiv., 547.

Tertiary Polyamines.—The procedures for preparing polyprimary amines again apply except that dimethylamine, morpholine and other secondary amines were used in place of ammonia. A typical product, prepared at 200° and 600 atm. pressure from a polyketone of 40% carbon monoxide content and dimethylamine was an amber, soft resin. It had the following composition.

Anal. C, 74.38; H, 11.80; N, 8.14; O (difference), 5.68; primary N, 0.72; neut. equiv., 218.

Characterization of Polyamines

Elementary Composition.—Standard analytical procedures were used to determine carbon, hydrogen, total nitrogen (Dumas) and primary amino nitrogen (Van Slyke). Oxygen was calculated by difference, and the remaining carbonyl content of the polyamines was calculated from this value. The values obtained for carbonyl are therefore subject to the cumulative errors of the carbon, hydrogen and nitrogen values and are not precise. It will be noted that even the "tertiary" polyamine contained a small proportion of primary amino nitrogen, and it is assumed that this was introduced by ammonia formed as a result of a certain degree of nickel-catalyzed disproportionation of the amine used.

Neutral Equivalent.—This was determined by perchloric acid titration in glacial acetic acid as solvent. Values up to the range 500–600 have been reliable and reproducible, while higher values have been taken as indicative only of order of magnitude. Acid solubility becomes incomplete in polyamines of neutralization equivalent more than about 600.

Molecular Weight.—This value was determined ebulliometrically in the same fashion as for the parent polyketones.[1]

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[4] H. H. Hoehn, U. S. Patent 2,495,255, January 24, 1950; C. H. Greenewalt, U. S. Patent 2,063,158, December 8, 1936.

Infrared Absorption Spectra.—The infrared absorption spectra were determined using a Perkin–Elmer model 21 recording infrared double-beam spectrophotometer. Specimens were prepared by melting and pressing the sample between two flat rock salt plates separated near their edges by metal shims approximately 1 mm. thick. The infrared determinations were made by Miss Doris Huck.

Derivatives of the Polyamines

Preparation of Polyamine Salts.[5] A.—These were prepared by the addition of the desired acid to a benzene solution of polyamine followed by removal of the solvent by vacuum distillation. For example, a polyamine of neutral equivalent 526 (27 g.) was treated with 85% lactic acid (5.9 g.) in benzene (100 ml.) to obtain a colorless, water-soluble, resinous lactate (30 g.). The lactate showed a saponification equivalent of 680. Similarly, a polyamine (25 g.) of neutral equivalent 515 was treated with 37% hydrochloric acid (5 ml.) in benzene (200 ml.), and the benzene and water were removed by distillation to obtain a gummy, reddish solid, difficultly soluble in water.

Anal. Calcd. for $(RNH_2) \cdot HCl$, where RNH_2 has neut. equiv., 515; Cl, 6.48. Found: Cl, 6.32.

B.—Salts of the polyamines with long chain acids have been made by metathesis of soluble polyamine salts with appropriate acid salts. For example, aqueous solutions of the acetate of a polyamine of neutral equivalent 523 and of sodium dodecyl sulfate were mixed in equivalent proportions. The poly-(dodecylammonium sulfate) precipitated immediately as an amber, tacky resin, which was dried in vacuum.

Anal. Calcd. for $RNH_2 \cdot HSO_4C_{12}H_{25}$, where RNH_2 has a neut. equiv. of 523; S, 4.14. Found: S, 3.25.

Preparation of a Polyquaternary Salt.[6]—A polytertiary amine (made from dimethylamine) of neutral equivalent 327 (34 g.) and benzyl chloride (13.2 g.) were allowed to stand in benzene solution (200 ml.) at room temperature for 24 hours. The benzene was then removed by vacuum distillation to obtain an amber-colored, glassy, water-soluble resin.

Anal. Calcd. for $R(CH_3)_2C_7H_7NCl$, where $RN(CH_3)_2$ has a neut. equiv. of 327; Cl, 7.8. Found: Cl, 6.0.

Preparation of a Polyamine Oxide.—A tertiary polyamine made with dimethylamine and having a neutral equivalent of 327 (25 g.) was treated with 30% hydrogen peroxide (28 ml.) in 3:1 isopropyl alcohol:water (200 ml.) at 70° for seven hours. The resulting solution was evaporated to dryness on the steam-bath to obtain a colorless, tacky resin, which readily oxidized aqueous potassium iodide solutions.

Anal. C, 72.54; H, 12.23; N, 3.63; O (difference), 11.60; neut. equiv., 458.

Preparation of a Polyamide.—A polyprimary amine of neutral equivalent 523 (54 g.) and an equivalent quantity of stearic acid (29 g.) were heated in refluxing xylene (50 ml.) at 165–200°. The water formed was removed by azeotropic distillation and was collected in a conventional liquid separator. When evolution of water was complete (7.5 hours), the xylene was removed by vacuum distillation to obtain a hard wax, insoluble in dilute acid and alkali. The acid number of the product was found to be 0.8, showing that the amidation was essentially complete.

Preparation of a Polyurea.[7]—A solution of potassium cyanate (9.75 g.) in water (40 ml.) was added with stirring to a solution of a polyprimary amine of neutral equivalent 515 (54 g.) in 400 ml. of water containing 7.2 ml. of glacial acetic acid. A gummy mass of the desired polyurea formed during the addition. After about an hour of stirring, the mass hardened and broke into solid, somewhat tacky granules. The polyurea was filtered off by suction and was dried in vacuum over concentrated sulfuric acid.

Anal. Calcd. for $RNHCONH_2$, where RNH_2 has a neut. equiv. of 515; N, 5.02. Found: N, 5.17.

The polyurea was insoluble in water but was soluble in isopropyl alcohol. Addition of a small amount of 37% formaldehyde to an isopropyl alcohol solution of the polyurea caused immediate precipitation of an insoluble, facticelike resin.

Preparation of a Polythiourea.—A polyprimary amine of neutral equivalent 523 was treated with a slight excess of ammonium thiocyanate as in the previous experiment. The resulting polythiourea was obtained as an amber-colored, tacky resin.

Anal. Calcd. for $RNHCSNH_2$, where RNH_2 has a neut. equiv. of 523; N, 4.81; S, 5.5. Found: N, 4.61; S, 4.57.

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[5] M. E. Cupery, U. S. Patent 2,579,033, December 18, 1951.

[6] D. D. Coffman, U. S. Patent 2,595,225, May 6, 1952.

[7] J. T. Maynard, U. S. Patent 2,595,400, May 6, 1952.

WILMINGTON, DELAWARE

[CONTRIBUTION FROM HERCULES EXPERIMENT STATION, HERCULES POWDER COMPANY]

The Synthesis and Polymerization of Ethylenesulfonic Acid

BY DAVID S. BRESLOW AND GEORGE E. HULSE

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Ethylenesulfonic acid has been prepared by saturating an aqueous solution of sodium ethylenesulfonate with hydrogen chloride, separating precipitated sodium chloride, and distilling the free acid. It polymerizes readily in aqueous solution in the presence of free-radical catalysts or when exposed to ultraviolet light. Both the rate of polymerization and the molecular weights of the polymers are increased with increased monomer concentration. Ethylenesulfonic acid copolymerizes slowly with methyl acrylate and with acrylonitrile.

Only two syntheses of ethylenesulfonic acid, $CH_2{=}CHSO_3H$, are reported in the literature, the classical procedure of heating 1,2-ethanedisulfonyl chloride[1] and, more recently, the dehydration of sodium 2-hydroxyethanesulfonate with polyphosphoric acid.[2] It has now been found that ethylenesulfonic acid can be prepared in good yields from sodium ethylenesulfonate.[3]

The preparation of ethylenesulfonic acid from sodium ethylenesulfonate is based on the low solubility of sodium chloride in concentrated aqueous hydrochloric acid. A solution of sodium ethylenesulfonate was saturated in the cold with hydrogen chloride; sodium chloride was filtered off, and the filtrate was distilled. A 74% yield of crude ethylenesulfonic acid was obtained, redistillation giving a 66% yield of pure acid.

The literature on the polymerization of ethylenesulfonic acid and its derivatives has been summarized recently.[4] Alderman and Hanford[5] reported that ethylenesulfonic acid polymerized in bulk very slowly to a dark-colored, rubbery polymer when

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[1] E. P. Kohler, *Am. Chem. J.*, **19**, 728 (1897); **20**, 680 (1898).

[2] J. A. Anthes and J. R. Dudley, U. S. Patent 2,597,696 (1952).

[3] D. S. Breslow, R. R. Hough and J. T. Fairclough, THIS JOURNAL, **76**, 5361 (1954).

[4] C. E. Schildknecht, "Vinyl and Related Polymers," John Wiley and Sons, Inc., New York, N. Y., 1952, pp. 643–648.

[5] V. V. Alderman and W. E. Hanford, U. S. Patent 2,348,705 (1944).