THE NITRATION OF POLYAMIDES

A Thesis

by

Melvin Jonathon Smith

Submitted to the Faculty of Graduate
Studies and Research in partial fulfilment of the requirements for the
degree of Master of Science

McGill University

September 1945

The author wishes to acknowledge with thanks the generous assistance of Dr. R.V.V. Nicholls, under whose direction this investigation was undertaken, and the valuable suggestions of Dr. S.A.V. Deans, of Canadian Industries Limited.

TABLE OF CONTENTS

Page

I HISTORICAL REVIEW

II EXPERIMENTAL PROCEDURES AND DISCUSSION OF RESULTS

Master of Science Department of Chemistry

Melvin Jonathon Smith

THE NITRATION OF POLYAMIDES

This investigation was undertaken in an attempt to prepare an explosive with certain satisfactory plastic and adhesive properties. It seemed most likely that these properties would be obtained in a nitrated polymeric compound. The polyamides of succinic, malic, and tartaric acids were prepared, and the products of their nitration were investigated.

It was found that a satisfactory succinic acid - ethylene diamine polymer could be prepared, and could easily be nitrated. The product, though possessive of detonating qualities, was not adequately stable for use as a military explosive. Difficulties were encountered in the preparation of satisfactory polymers from malic and tartaric acids with ethylene diamine, due to the presence of the substituent hydroxy groups. However, an interesting and original study of the relative behaviour of these compounds was made.

GENERAL INTRODUCTION

In the course of the Second World War there developed a need for an explosive which would have certain plastic and adhesive properties. In particular, such a substance would be useful for demolition charges, since it could be molded as required; as a rocket propellent, since it would adhere to the wall of the container and hence burn smoothly and uniformly; and in fuses, since uniform extruded filiaments which would burn at a controlled rate could be obtained.

Certain moldable explosives, such as plastic TNT and RDX, were well known. However, these consisted of an active agent mixed with an inert plasticizer, and the diluent tended to impair the explosive power. It was thought possible that a single substance, such as a highly nitrated polymeric compound, would combine the required properties of explosiveness and moldability.

It was known that certain monomeric nitrated amides had been prepared, and were explosives of high power, though far too unstable to be of practical use. It was deemed worthwhile to attempt to combine this great explosive power of nitrated amide linkages with the known stability of linear polyamide chains in order to obtain a product satisfactory in both respects.

This would, moreover, be in keeping with the modern trends in explosive synthesis with regard to structure. the organic compounds first used for that purpose, such as picric acid and TNT, had the all-important nitro groups attached directly to carbon atoms, usually in the benzene nucleus. Later, compounds with nitro groups attached to oxygen atoms, such as glycerine trinitrate (nitroglycerine), were used. However, the most recently developed explosives, such as RDX and NENO, and also the well-known tetryl, possess nitro groups attached directly to nitrogen atoms. Nitrated polyamides, if formed from unsubstituted monomers, would possess the nitro-nitrogen (nitramine) linkage; if formed from hydroxyl group substituted monomers they would possess both the nitramine and the nitro-oxygen (nitrate) linkage. It was decided to attempt to prepare both types of compounds.

The investigations of this thesis concern polyamides of a type not usually studied because of their unsuitability for use as synthetic fibres. They are the condensation products of ethylene diamine with succinic, malic, and tartaric acids. The latter two compounds are, of course, mono and di-hydroxy substituted dicarboxylic acids. In these polyamides, the number of atoms per basic unit is eight; W.H. Carothers' minimum for practical synthetic fibres is "greater than eight" (50). However, the short repeating unit permits the optimum degree of nitration, which is the critical factor in the synthesis of explosives.

No records whatsoever were discovered of the previous preparation or nitration of the polyamides of malic or tartaric acids with ethylene diamine or any other amine; or of the nitration or attempted nitration of the succinic acid polymer. The latter substance, however, is quite well known (84).

HISTORICAL REVIEW OF MACROMOLECULAR COMPOUNDS AND OF POLYAMIDES IN PARTICULAR

Polymeric compounds have been known almost since the dawn of systematic organic chemistry. Numerous chemists of the old tradition made them accidentally while searching for new crystalline substances, and discarded them as useless. For instance, Simon prepared polystyrene in 1839 (1), and Baeyer made several resins from benzaldehyde and phenol (2). Invariably, these materials were not deemed worthy of further investigation.

The first macromolecular compound to be studied by science was nitrocellulose, which was discovered by Shönbein and Böttcher in 1846. Shonbein sent some optically clear samples to Faraday and the latter, much impressed, suggested their use as mechanical articles. "Celluloid" was popularized by John Hyatt, in America, soon afterwards.

In 1909, Dr. Leo Baekeland made his classical synthesis of a phenol-formaldehyde co-polymer (3), the first true synthetic resin of industrial importance. His ammonia catalyst was later modified to hexamethylenetetramine and even acids. The phenol component was shown afterwards to be replaceable by naphthol (4), and the formaldehyde by 2-dichloromethyl ether (5) to give Bakelite-like resins.

By the end of the First World War the search for new "plastic" materials was intense. In general, this took place along three parallel lines. First in industrial importance among the true synthetics were the polycondensates. These were materials of comparatively low molecular weight (up to 10,000), formed by a series of condensation reactions involving the elimination of certain by-products, such as water, alcohol, or a phenol. Usually, the interaction of two different compounds was necessary, although polycondensates may be obtained from the intermolecular reaction of one bifunctional compound, such a long-chain aliphatic amino acid.

Polycondensates are usually thermosetting, i.e., on the application of heat and pressure they become permanently infusible and insoluble. This is usually due to the setting-up of secondary cross-linkages. Important examples of industrial polycondensates include the urea-formaldehyde resins (6), whose excellent optical characteristics had given them a leading place among all commercial plastics by 1933; the phenol-aldehyde polymers, such as the already-mentioned Bakelite, the thioureas (7), and the alkyd resins (63).

The other major sub-group of synthetic polymers is the true, or addition polymers. These are usually formed from unsaturated monomers by simple repeated addition, and their average molecular weight is in general somewhat higher than that of the polycondensates, in the range 10,000 to 100,000. They rank far below the polycondensates in industrial importance. They are usually thermoplastic, i.e., they do not "set" or become permanently infusible on the application of heat and pressure. Industrial true polymers, in addition to polystyrene, include polyvinyl alcohol (60), polyvinyl acetate (61), polyvinyl chloride (83), the polyvinyl acetals (62), the polyacrylates (64), the indenes (9), and the coumarones (8).

To an increasing degree co-polymers are being synthesized, which combine the desireable properties of two or more monomerically derived products. Two outstanding examples are the polyvinyl chloride - polyvinyl acetate plastics, and the butadiene-styrene elastomers.

Naturally-occurring macro-molecular materials have been adapted, as have the synthetic, for practical use by investigators. These were usually cellulose derivatives. Nitrocellulose has already been mentioned, and cellulose acetate is at present an important commercial polymer.

Probably due to their great inertness and insolubility, polyamides have not been investigated as potential synthetic materials until comparatively recently (1930's). The first investigations were made by Wallace Hume Carothers, who dominated the field until his death in 1937. His first polyamides were prepared by the intermolecular condensation of 6-aminocaproic acid, on simple heating (45). About twenty per-cent of the seven-membered cyclic lactam is formed simultaneously. It is interesting to observe that under the same conditions, 4-aminobutyric acid and 5-aminovaleric acid yield the corresponding 5 and 6 membered lactams only. No polymer is formed. On the other hand, the reaction of 7 carbon-membered 7-aminoheptoic acid with itself is exclusively intermolecular. No lactam is formed. Evidently the steric factors tending to each type of reaction reach a critical state in the 6-membered chain.

The polymeric products were hard grey waxes, insoluble in all common organic solvents, but soluble in hot formamide and hot phenol. The cryoscopically-obtained molecular weights were in the range 800-1200. The end-group structure was indeterminate.

Later, Carothers and his co-workers devised a low-mean-free-path molecular still by means of which the molecular weights of condensation polymers could be increased to 20,000 or higher (46). This was particularly useful in the case of polyamides, as it improved their tensile strength to the point where use as a synthetic fibre was possible. The external appearance of the material, and some of its characteristic properties, were also changed quite markedly (47).

Using this technique, Carothers endeavoured to make industrially useful filiaments from molecularly distilled, cold-drawn superpolyamides formed intermolecularly from 8-aminocaprilic acid, 11-aminoundecanoic acid, and 17-aminoheptadecanoic acid, as well as the 6-aminocaproic acid (49). In many cases the starting material was the ethyl ester, rather than the free acid, with evolution of ethanol. The minimum molecular weights obtained are placed at 10,000, although exact estimations were difficult because of unfavourable solubility characteristics. X-ray diffraction tests showed the cold-drawn, extruded filiaments to be true fibres, possessing a very high degree of orientation of the macromolecules.

Meanwhile, in 1931, another method of synthesizing polyamides had been devised (48). Organic diamines were treated directly with dicarboxylic acids, or amide-forming derivatives of dibasic acids, such as the esters. The water or alcohol by-products were removed under vacuum. Still another modification was proposed in 1938. Carothers, in a patent published on his behalf after his death (50), proposed that this type of polymer could conveniently be prepared by condensing the salt, or simple monomeric amide, of a diamine and a dicarboxylic acid. The salt could easily be formed in alcohol solution. By preliminary purification of the salt, exact equimolecular ratios of diamine and dibasic acid would be obtained, and this was known to facilitate high molecular weight polymerization.

Actually, certain diamine-dicarboxylic acid salts had been known long before the work of Carothers, such as those derived from octamethylenediamine and oxalic acid (51), or from ethylene diamine and succinic acid (52). However, these were "of little or no utility as intermediates in the formation of fibre-forming polyamides". The dibasic acids actually used for polymer synthesis included those aliphatics of chain length, including carbon in the carboxyl groups, of 2 to 10, 13, 14, 18; p-phenylene diacetic; 1,4-dicarboxycyclohexane; and 1,3-dicarboxycyclopentane. Diamines used included ethylene, propylene, butylene, 1,3-diaminobutane; tri, tetra, penta, hexa, deca, trideca, and octadeca methylene; p-xylylene and cyclohexylene.

In all of Carothers' subsequent patents (53,54), polyamides were made exclusively through salt intermediates. Usually the salt was isolated, although occasionally it was condensed in solution. In order to avoid oxidation, heating was carried out under an inert atmosphere. It is definitely stated that for fibre forming qualities the carbon chain length of the diamine and of the dicarboxylic acid must be at least four.

Baker and Fuller have studied the structure and the relation of physical properties to structure of linear polyamides (55). Their methods were X-ray diffraction patterns, elastic moduli, and moisture sorption. The results indicated that certain hydrogen-bonded dipole layers formed by association of polar linkages in adjacent chains governed physical properties. Melting point, hardness, elastic modulus, and moisture sorption phenomena could all be explained by this concept. The generalized conclusion was made that macromolecular solids containing some crystalline regularity could be treated as defect (physical) systems in which, nevertheless, relatively simple factors, such as the position and organization of interacting polar groups governed physical properties.

Similar studies were made by the same investigators on N-methylated linear polyamides, using essentially the same techniques (56). X-ray results indicated a retraction of the N-methylated chains by partial folding along the fibre axis, to yield kinked instead of straight chains. The observed rapid decrease upon methylation of elastic modulus and hardness, and the increase in solubility and in moisture sorption are explained by the decline of hydrogen-bonding and the general disorder. An interesting suggestion is that the chain retraction and extention observed may be the first stages of rubbery elasticity.

Hess and Kiessig (57) calculated unexpectedly small apparent molecular weights from their X-ray diagrams. They suggest that the reflections observed really represent micellar regularities, with length of crystal areas smaller than molecular lengths. They estimated the length of crystal areas from electron diffraction diagrams at about 100 A.

The very important question of reliable molecular weights was attacked by Staudinger and Jörder in an excellent paper (58). Specific constants for Staudinger's standard equations were obtained to make possible viscometric chain-length determinations in m-cresol, an adequate solvent for superpolyamides. It was again found that the molecular weights were relatively low (eg. - 12,400) considering the remarkable tenacity and great practical usefulness of the fibres. However, Staudinger supports H. Stock's criticism of the assumption (see above) that the great strength of polyamide fibres is due to cross-linkages at right angles to the fibre axis, brought about by residual valences between polar -CO groups and polar -NH groups. Stock was able to obtain fibres of considerable tenacity from relatively short-chain superpolyesters. High tenacity may possibly be due to special spinning conditions. Carothers had already demonstrated the extraordinary orientation produced by cold-drawing, and it is well known that tensile strength is highly dependent on molecular orientation.

A. Matthes, in his chain-length investigation on German commercial nylons, used both viscometric and end-group estimation methods (59). The latter involved the use of the van Slyke technique for the determination of amino nitrogen, and seemed to give satisfactory results. (This would seem to contradict Carothers' early assumption (45) that pyrolysis during preparation would make end-group estimations impossible.) The viscosity measurements were made in 40% and in concentrated sulfuric acid, on relatively low molecular weight materials. The results obtained by extrapolation of the molecular weight versus viscosity curves to high molecular weights were checked by a study of depolymerization kinetics in dilute acid. Matthes interpreted his results as indicating that polyamide molecules IN SOLUTION were unbranched but highly curled up.

HISTORICAL REVIEW OF EXPLOSIVES IN GENERAL

The history of explosives is a long and interesting one. Black powder, an intimate mixture of an oxidizing and a reducing agent - saltpeter plus sulfur and charcoal - was known since the beginning of the thirteenth century. Traditionally, the discovery was made by a monk of Freiburg, Germany, who later was ostracized for aiding the "work of the devil". For six hundred years, until the middle of the nineteenth century, black powder or minor variations thereof was used almost exclusively. Antimony sufide, copper acetate, and potassium chlorate, variously mixed with gunpowder, found occasional use in pyrotechnics (10, 11). From the simultaneous discovery by Shönbein and Böttcher in 1846 of nitrocellulose, and of nitroglycerin by Sobrero in the same year dates the modern period in explosives.

The outstanding characteristic of an explosive is, of course, its extraordinarily rapid rate of combustion upon ignition, or detonation, with the accompanying formation of large quantities of hot gas. In black powder the rate of combustion was limited by the degree of intimacy of the mechanical mixture of oxidizing and reducing agents. All later explosives contain both essential agents in more-or-less firm chemical combination on the same molecule, a very much greater degree of intimacy. Usually, loosely held oxygen, as in nitro groups, functions as the oxidizing agent, and the carbon or nitrogen atoms of the remainder of the molecule as the reducing agent. Variations in structure on this theme are possible only in organic compounds, and the rise of organic chemistry in the nineteenth century closely parallels the development of modern explosives. An interesting parallel is the twentieth century rise of nuclear physics, which has culminated in the atomic bomb.

A side problem is that of ignition, or detonation. Black powder, very insensitive to percussion, was set off by a flame. Organic nitrates behave in opposite manner. Nitroglycerine burns quietly, but slight percussion will cause it to explode. Alfred Nobel, who first absorbed nitroglycerin in kieselguhr to make dynamite, also made the first detonators. He used black powder in a metal or glass container, connected to a safety fuse. This was used to explode liquid nitroglycerin, but was crude and unsatisfactory. Later, he used mercury fulminate (12), which was soon universally adopted under his patent, although the compound had been suggested for this purpose by Wright in 1823.

For quite some time, no attempt was made to detonate other organic compounds by means of the mercury fulminate cap, although many compounds later to be used as powerful explosives were quite well known at the time. Dynamite and nitrocellulose were in constant and universal use.

Finally, in 1871, Sprengel suggested pure picric acid as an "ideal" smokeless explosive (13), although credit is commonly given to Turpin, who popularized the idea and held the French and German patents (14). The stability and other advantages of this compound made possible the first artillery shells. However, the easy formation of very sensitive metallic picrates while in contact with the shell wall caused disastrous accidents, and eventually led to the abandonment of this material as an explosive for any purpose.

Analagous compounds were postulated as substitutes, and for a time trinitrocresol and cresylite, a mixture of picric acid and trinitrocresol, were used. However, the emergence of the contact process for the manufacture of cheap sulfuric acid on a large scale in 1900 made possible the extensive use of trinitrotoluene. Trinitrobenzene, though a superior explosive, is far too difficult to prepare.

The materials used as explosives at this time were by no means always pure compounds. Many mixtures were used, practically all of which incorporated either ammonium nitrate or glycerol trinitrate as major ingredients. A typical example is Ammonol, a popular Austrian explosive in the period 1905-1918, which consisted of ammonium nitrate, TNT, carbon, and aluminum. Of course, all dynamites are mixtures.

Of the hundreds of aromatic nitro compounds investigated for this purpose (41) trinitrotoluene was by far the most successful. It combined great power with ease of preparation, chemical inertness, absolute stability, and insensitivity to accidental detonation, all of which are essential qualities in any explosive.

The list of nitric esters (possessing $O-NO_2$ linkages) that have been investigated is very long (41). Both aliphatic and aromatic compounds are included. Glycerol trinitrate and nitrocellulose are outstanding, of course. Nor was RDX the first nitro-nitrogen, or nitramine-type compound to be utilized. Others include nitroguanidine, urea nitrate, nitroamide, and ethylenedinitramine. Finally, fulminates and azides were found to be particularly useful as detonators. Of these, the most successful were mercury and silver fulminate, and lead and silver azide.

Of minor importance are various chlorate and perchlorate explosives. These are usually mixed with dinitrotoluene and diluents such as wood-pulp or flour, and their period of popularity has been brief. (40).

An important component of most explosives not hitherto mentioned is the stabilizer. It has been shown that all explosives evolve more-or-less gas continuously in accordance with an equation with specific constants for each substance (42). The rates of evolution vary from 86,000 cc/kg./hour for glycerol trinitrate to 0 cc./kg./hour for 1,3,5-trinitrobenzene, both at 140°. TNT yields 0.8 to

1.8 cc./g. in 100 hours at 140°. The gases evolved are oxygen, nitrogen, carbon monoxide, carbon dioxide, and various oxides of nitrogen.

This phenomenon may lead to autocatalytic decomposition. In order to be effective, a stabilizer must have the ability to form a uniform solution or sol with the explosive, absorb gaseous oxides of nitrogen, and neutralize any acid present. Fulfilling these conditions, the stabilizer must yet be sufficiently inactive not to attack the explosive. Diphenyl amine is the best all-round stabilizer known, but it is not a solvent for nitrocellulose and is yet too active for glycerol trinitrate. It is found that centralite, an ethyl phenyl substituted urea, is most satisfactory for nitric esters (43).

RECENT INVESTIGATIONS OF EXPLOSIVE POLYMERS AND NITRAMINE TYPE COMPOUNDS

In view of the extensive experimental work recently carried out in this field, only a brief outline of the results can be given here.

An investigation was made at McGill University of the polyester derived from ethylene glycol and tartaric acid (65). The nitrate was prepared, but was found to be unstable. The nitration of polyethylene malate gave a flocculent precipitate which was likewise difficult to purify and unstable (66). Some cross-linking also took place between the long molecules (68). An attempt to prepare a mixed polyester-polyamide suitable for nitration by the condensation of ethanolamine with a dicarboxylic acid, was abandoned (67). In general, experience of other workers seems to have shown that compounds having a hydroxy group on the carbon atom adjacent to a carbonyl group give unstable nitrates (66).

A stable polyvinyl nitrate has been prepared from low residual-acetate containing polyvinyl alcohol by Dr. R.H. Clark at the University of British Columbia (65). Nitroethylene has been prepared and polymerized (85), and considerable interest has been shown in certain nitroindede polymers. Nitroguanidine has successfully been condensed with formaldehyde to yield a polymeric explosive in the form of a lyophilic colloid (80). However, indecisive results were obtained in attempts to prepare an explosive polymer from lignin wastes (66).

Certain polymers resulting from the action of oxidizing agents on nitrated amines, and from the condensation of formaldehyde with nitrated amines and nitroparaffins were investigated by Urbanski and his English co-workers, in a search for satisfactory fuse powders. (69). Materials resulting from the nitration of commercial dyestuffs were also prepared. The products were not altogether satisfactory for the purpose in mind, however, as they left a solid residue on burning. They were quite interesting, however, from a theoretical point of view.

H. A. Bruson, at Röhm and Haas, Philadelphia, has reported very extensive work on the preparation of polymers which may be of interest as explosives (70). Hundreds of new compounds were prepared in an attempt to find an explosive with satisfactory plastic and adhesive properties. The project can only briefly be outlined here. No data are available on the explosive properties of any of the products.

Nitroparaffins were condensed with various aldehydes to give resins which burned with great vigour (71).

The condensation of trinitrotoluene with formaldehyde and/or various primary and secondary amines, such as diethanol amine, dimethyl amine, piperidine, and morpholine, was carefully studied (72, 73). The most promising product was trinitrophenyl ethanol (1-hydroxy, 2-trinitrophenyl ethane), formed from TNT and aqueous formaldehyde. It was esterified with polybasic acids and with other polymerizeable groups (acrylyl, methacrylyl, crotonyl, etc.) and later condensed.

A material was prepared which was apparently the polymer of 2,4,6-trinitrostyrene (74).

A number of nitrated aromatic amines were formed by substituting the hydroxyl group of trinitrophenyl ethanol for NR_2 groups. The picrates of these amines were also made, by direct treatment with picric acid in suitable solvents. It was, of course, planned to tie on polymerizeable groups (75).

Some nitro-alkyl acrylates and methacrylates were prepared (76).

Various esters containing nitro groups and certain polymerizeable groups were made (76).

Ethyl methacrylate was copolymerized with 2,4,6-trinitrophenyl methacrylate to form a hard resin (76), and many nitro-ether type derivatives of phenolic resins were made (76, 73).

Many nitric esters were prepared that contained polymerizeable groups, such as allyl nitroalkyl maleates, methallyl nitroalkyl maleates, nitroalkyl maleates, allyl 3,5-dinitrobenzoate, monoallyl maleic acid, and monomethallyl maleic acid (77).

The reaction of amines and formaldehyde with nitro compounds was investigated (72).

Several nitro-group containing, olefin type compounds were polymerized (72).

A phenol-type resin was formed from o-cresol, formaldehyde, and 2,4-dinitrochlorobenzene, and was nitrated successfully (78). Several low-melting polynitrophenyl ethers were prepared after previous high-melting analagous compounds had been found to be unsatisfactory (78).

Finally, trinitrophenyl ethanol was condensed with various chlorides and acid anhydrides (79) to give resins.

The products mentioned above are those thought by Bruson to be most promising, and were given corresponding emphasis in his reports. About January 15, 1944, the project was either abandoned, or else it was decided no longer to publish the reports.

During the present war, new explosives, eg. RDX, NENO, have been developed containing the nitramine and also nitramide ($-CO-N-NO_2$) groups. A confidential C.I.L. report (44) outlines an attempt to synthesize other possible explosives containing the latter type of linkage. The N-substituted amides of hydroxy acids - glycolic, lactic, glyceric, gluconic, tartronic, tartaric, and mucic - were prepared and nitrated. Theoretically, the products would contain both nitroxy and nitramide groups.

In the majority of cases (seven) nitration was complete and yielded products of explosive power greater than TNT (up to 134% TNT). Some were fairly sensitive to impact. However, all had a very poor thermal stability and all the nitroxy-nitramides (the fully nitrated products) were found to be subject to hydrolysis while in contact with water at room temperature. The nitroxy-amides, with one exception, also showed appreciable hydrolysis. It was thus concluded that, despite their high power, these substances would not be suitable as explosives.

It was at this stage that it was decided to proceed with the nitration of polyamides in these laboratories.

EXPERIMENTAL - PREPARATION OF POLYAMIDES

The best commercial reagents were purified as much as possible, the ethylene diamine by careful distillation in an all-glass apparatus, and the succinic, malic, and tartaric acids by repeated recrystallization from suitable solvents. The melting and boiling points were checked against standard data.

Preparation of Polyamides by the Direct Method

General:

Five-tenths mole ethylene diamine was added slowly to an equivalent quantity of dicarboxylic acid in a flask equipped with a reflux condenser. The reaction was vigorously exothermic. The mixture was heated by means of an oil bath until a homogeneous melt resulted, and then refluxed for twelve hours. An inert atmosphere was provided by a stream of deoxygenated nitrogen, which was obtained by passing commercial nitrogen through two gas-washing bottles filled with alkaline pyrogallol, and then through a sodium hydroxide-filled drying tube.

The condenser was then changed to a position for normal distillation, and the mixture was heated under nitrogen at 135° to 250°, depending on its stability. This was continued until water was no longer evolved, and for one hour thereafter. After cooling, the products were removed and purified as described subsequently.

Succinic acid and ethylene diamine:

The ideal temperature of reflux was 145° to 155°. The final heating was carried out under reduced pressure, at 250°. Heating to 290° resulted in great discoloration.

The product was a hard, light brown coloured, largely homogeneous amorphous solid, which was powdered with some difficulty. The crude yield was 98%. The material was insoluble in water and in all common organic solvents. It was moderately soluble in hot phenol and hot formamide.

Purification was attempted by extensive washing of the powdered material with boiling water. A white crystalline material was recovered in small amounts from the washings, which melted at 255°, and was extensively soluble in water at 75°- 80°. The same material was obtained in all (succinic) preparations by this method.

The purified product did not melt below 320°, but showed signs of decomposition at 300°in the presence of air.

Anal. Calcd. for $(C_6H_{10}O_2N_2)_n$: N, 19.70.

Found 19.48, 19.38.

Carothers had estimated the molecular wieght of polyamides prepared in this manner at 1000 - 3000. This was not verified, however.

Malic acid and ethylene diamine:

On refluxing at 135°, a heavy viscous liquid was obtained, which upon drying turned into an optically clear, light-brown solid. It was necessary to dry not above 80° in the presence of oxygen, in order to avoid oxidation. The product was very soluble in water, but was insoluble in organic solvents. It was purified by twice dissolving in water and precipitating with acetone. The powdered material was highly deliquescent. The melting point was 95° and at 135° decomposition with gas evolution commenced.

Anal. Calcd. for $(C_6H_{10}O_3N_2)_n$: N, 17.71

Obtained 16.51, 16.42.

This low figure can be accounted for by the postulated low molecular weight of this polymer (see discussion), which would decrease the theoretical proportion of nitrogen; and possibly by powerfully adsorbed water.

Tartaric acid and ethylene diamine:

Upon refluxing at the minimum possible temperature, 170°, a somewhat discoloured heavy viscous liquid was obtained, which dried to a dark brittle solid at 110°. The powdered solid was soluble in water and insoluble in common organic solvents, but not nearly so hygroscopic as the malic acid product above. The melting point was 100°, and decomposition with gas evolution commenced at 135°.

Anal. Calcd. for $(C_6H_{12}O_4N_2)_n$: N, 14.60.
Found 13,60, 13.76.

This low result may also be accounted for by inadequate polymerization (see discussion).

Preparation of Polyamides by the Salt Intermediate Method

General:

Two-tenths mole dicarboxylic acid was dissolwed with heating in methanol so as to yield approximately a 20% solution. An equivalent quantity of ethylene diamine was diluted with methanol to a similar concentration. The amine solution was added slowly to that of the acid with stirring with the immediate formation of a dense white precipitate. The reaction was highly exothermic. The crystalline salt was filtered, washed with a little methanol, recrystallized from a water-methanol mixture, and dried at room temperature in a vacuum desiccator.

The salts with ethylene diamine of succinic, malic, and tartaric acids were all thus prepared. They were all extensively soluble in water, and insoluble in methanol and all common organic solvents. Solubility seemed to be less in hot methanol than in cold. The salts dissolved somewhat in ethylene diamine.

Approximately 10 g. of salt was placed in a thick-walled Pyrex bomb tube about 20 mm. in diameter by 20 cm. long, and tamped down firmly. The constriction near the entrance of the tube was narrowed to about 2 mm. The tube was connected to a train supplying oxygen-free nitrogen, and alternatively to a vacuum pump via a three-way stopcock. A pressure gauge was included in the apparatus. The tube was evacuated and filled with deoxygenated nitrogen three times, this being deemed adequate to remove all oxygen. The system was placed under slight vacuum, and the tube sealed off at its constricted neck.

The sealed tube was then placed in a gas-fired bomb furnace, and heated above the melting point of the salt one hour (at 200° for the succinic salt, 160° for the malic and tartaric salts.) Especial care was taken with the malic and tartaric salts as these tended to decompose at 15° or 20° above their melting points.

After cooling the tube was carefully opened, sealed to a delivery tube, and connected via an ordinary distilling flask trap and a dry ice trap to the nitrogen-vacuum apparatus. The partially condensed salt was then heated under nitrogen at one atmosphere and at 200° for one hour, and finally, under vacuum, at 250° for one hour. The tube was evacuated gradually in order to reduce the danger of frothing. The final pressure was in the neighborhood of 2 mm. of mercury. The product was cooled under nitrogen and removed by breaking the tube.

Succinic acid and ethylene diamine:

The melting point of the salt was 190°.

Anal. Calcd. for $C_6H_{12}O_3N_2$: N, 17.50.

Found 17,41, 17.30.

In the condensation, if the final heating is at 275°, a highly discoloured material results. If at 250°, the product is only slightly off-colour (light brown).

Anal. Calcd. for $(C_6H_{10}O_2N_2)_n$: N, 19.70.

Found 19.46, 19.58.

The polyamide was powdered and purified by washing with hot water. As expected, it was amorphous, infusible and soluble only in hot formamide and hot phenol.

Malic acid and ethylene diamine:

The melting point of the salt was 161°. In air, it decomposed rapidly above its melting point. The maximum temperature of condensation was 250°.

Anal. Calcd. for $C_6H_{12}O_4N_2$: N, 15.90.

Found 15.63, 15.68.

The product, after cooling, was in the form of small, translucent, yellow-red flakes. These were completely insoluble in water and all organic solvents and also in phenol and formamide. No melting point was observed below 300°.

Anal. Calcd. for linear polyamide $(C_6H_{10}O_3N_2)_n$: N, 17.71.

Found, 17.66, 17.69.

Tartaric acid and ethylene diamine:

The salt melts at 156° and decomposes at 170° in the presence of air.

Anal. Calcd. for $C_6H_{12}O_4N_2$: N, 14.60.

Found 14.22, 14.34

The maximum temperature of condensation was 255°. The physical appearance of the product was remarkably like that of the malic acid polymer described above. Its general properties were also identical, i.e., it was completely infusible and insoluble.

Anal. Calcd. for linear polyamide $(C_6H_{10}O_4N_2)_n$: N, 16.07.

Found 15.80, 15.79.

DISCUSSION OF RESULTS

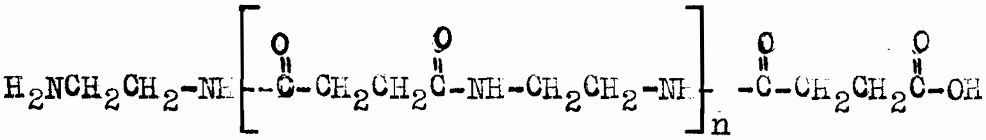
The two methods of polyamide preparation used yielded, in general, significantly different products. These will be dealt with individually.

Preparation of Polyamides by the Direct Method

Succinic Acid and ethylene diamine:

The observed physical and chemical properties of this product are just those to be expected of an unsubstituted straight-chain polyamide of moderate molecular weight. The amorphous appearance, infusibility, and highly specific solubility behaviour are all very characteristic.

The expected molecular structure is then



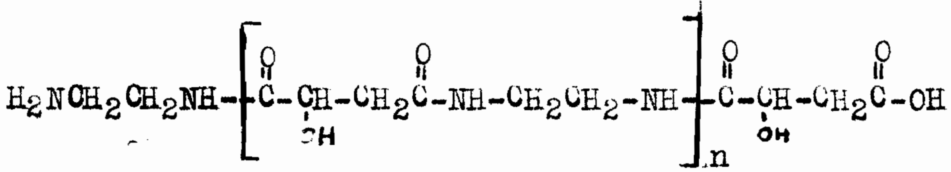
$$H_2NCH_2CH_2-NH\left[-\overset{O}{\overset{\|}{C}}-CH_2CH_2\overset{O}{\overset{\|}{C}}-NH-CH_2CH_2-NH-\right]_n-\overset{O}{\overset{\|}{C}}-CH_2CH_2\overset{O}{\overset{\|}{C}}-OH$$

where "n" is the degree of polymerization of the basic structural unit, For a molecular weight of 1000 - 3000, "n" equals 7 to 20.

The water-soluble byproduct that was recovered has, it will observed, a rather high melting point, viz. 255°. In view of the fact that the melting point of the salt, or mono-amide, is 187°, this may possibly be the tri or tetraamide. However, no further identification was attempted.

Malic acid and ethylene diamine:

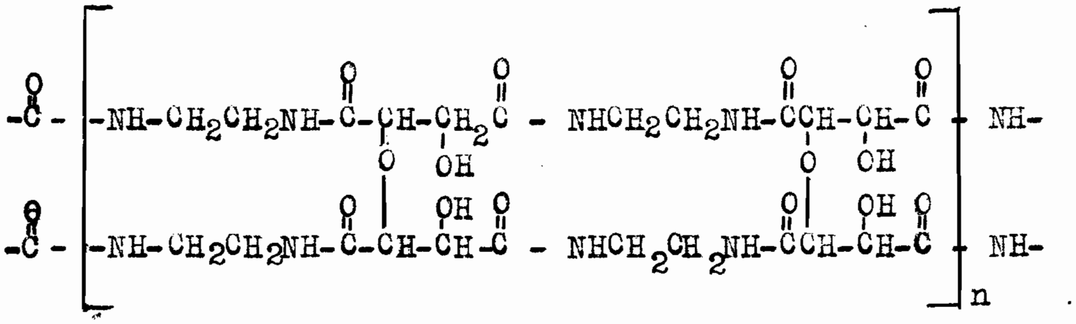
The outstanding characteristic of this substance is its great affinity for water. In view of the fact that the polymerized molecule contains only one hydroxy group per eight atoms of chain, it does not seem reasonable to assign this behavour entirely to the presence of the residual hydroxy groups. It seems likely that a considerable number of highly polar amino and carboxy groups still remain free. This would be the case had polymerization not proceeded to any great extent. This hypothesis is also favoured by the fact that the conditions of reaction had been relatively mild. Thus, in the tentative structure below, the degree of polymerization "n" is set arbitrarily at three to five.



$$H_2NCH_2CH_2NH-\left[\overset{O}{\overset{\|}{C}}-\underset{OH}{\underset{|}{CH}}-CH_2\overset{O}{\overset{\|}{C}}-NH-CH_2CH_2-NH-\right]_n\overset{O}{\overset{\|}{C}}-\underset{OH}{\underset{|}{CH}}-CH_2\overset{O}{\overset{\|}{C}}-OH$$

Tartaric acid and ethylene diamine:

Due to the large number of hydroxyl groups present, one would expect exaggerated solubility characteristics with respect to water. The absence of this, plus the extensive discolouration, suggests that at the high temperature of reflux a side reaction has taken place, leading to hydrogen bonded cross-linkages between molecules, i.e., to the structure



Kinetically, this would be highly probable relative to the chance of collision of a growing chain with an ethylene diamine or tartaric acid molecule. Even a relatively small degree of hydrogen bonding would be adequate greatly to increase the average molecular weight and modify the solubility characteristics.

Preparation of Polyamides by the Salt Intermediate Method

Succinic acid and ethylene diamine:

It is clear that this product is essentially similar to that produced by the direct method. This may be due to the fact that, in the alternative method, the infusibility of this particular polymide permitted final heating to a very high temperature (270°).

It was, of course, impossible to prepare the polyamide by heating under vacuum above its melting point, as Carothers repeatedly instructs. His fibre-forming compounds all have adequately low melting points, a property which can be related to the length of their basic units. In the following table (50) it will be noted that as the number of atoms per basic unit increases, the melting point of the corresponding polyamide decreases:

TABLE 1

POLYAMIDE FROM	M.P. OF POLYAMIDE
Propylene diamine & sebacic acid	220°
Pentamethylene diamine & sebacic acid	195°
& dodecamethylene dicarboxylic acid	170°
& hexadecamethylene dicarboxylic acid	167°

Carothers notes too that these melting points, and also solubility characteristics, are affected only to a very slight extent by changes in molecular weights (presumably above a low minimum.) The one determining factor is the length of the structural unit.

It would therefore be expected that the polyamides of this investigation, possessing small basic units of eight atoms, would have very high melting points, or none at all. This is confirmed.

Malic acid and ethylene diamine:

It is at once evident that this substance is very different from that formed from the same starting materials by the alternative method. There has been a change from deliquescence to complete insolubility in water; from facile melting to definite infusibility.

In explanation, the extensive formation of cross-linkages between linear molecules at the high temperature of condensation can be postulated. Such behaviour among hydroxy-substituted polymers is quite well known under these conditions, and the hydrogen bonds formed have stability approaching that of true inter-atomic linkages. The rigid three-dimensional lattice that would result from such a reaction would, in effect, create one giant molecule of a crystal, or flake. This would, of course, lead to complete insolubility and infusibility.

Tartaric acid and ethylene diamine:

The properties of this substance bear the same relation to those of the alternative product as the properties of the probably-cross-linked malic acid polymer b bear to those of the product of its alternative synthesis. The implications regarding structure are clear-cut, and the conclusion seems warranted that extensive cross-linking has also occurred here.

The experimental results obtained thus far, together with hypotheses suggested in the discussion, may be outlined in the following table:

TABLE 2

COMPARISON OF PROPERTIES OF POLYAMIDES

Polyamide derived from ethylene diamine and the following acids	Properties	
	Direct (Mild) Method Product "A"	Salt Intermediate (Drastic) Method Product "B"
Succinic Acid	Linear, infusible insoluble. Mol. Wt. 1000-3000	Linear, infusible, insoluble. Mol. Wt. 2000 - 5000.
Malic Acid	Linear, water-soluble. Low mol. wt. (300-500). Low melting point.	Cross-linked, insoluble, infusible. Mol. Wt. ?
Tartaric Acid	Somewhat cross-linked. Water-soluble. Low melting point. Low mol. wt. (?)	Cross-linked, insoluble, infusible. Mol. Wt. ?

EXPERIMENTAL - NITRATION OF POLYAMIDES

General:

For comparative purposes, two nitrating agents of different potency were used. They were, respectively, a mixture of commercial concentrated nitric acid with 60% of 95-98% acetic anhydride; and a mixture of fuming, i.e. 97-100%, nitric acid with 60% of 95-97% acetic anhydride. Five to ten grams of polyamide was nitrated in one operation, and in general a ten-molar excess of nitric acid over polyamide was used. The reaction was carried out at 0° to 5° in a round-bottomed, three-necked one liter flask equipped with a mercury sealed, motor-driven stirrer, a separatory funnel, and a thermometer.

The nitric acid was pre-cooled in an acetone-dry ice bath, and to it was added, slowly, about one-half of the required acetic anhydride. The temperature of the mixture was kept below 30°. After cooling to about -20°, the mixture was added rapidly to the polyamide in the flask. The flask itself was cooled by means of an ice-bath. The reaction mixture was stirred rapidly, and and remainder of the acetic anhydride, pre-cooled, was added slowly through the separatory funnel.

In successful nitrations the polyamide dissolved rapidly, in ten to twenty minutes. The nitrated product was obtained by pouring the solution into an appropriate precipitating agent, as described subsequently.

Nitrations with concentrated Nitric Acid and Acetic Anhydride

The succinic acid polymer (Product "A")

It was found that the polymer was soluble in the acid mixture at 0^{0}, but that no nitration was effected. The original material was recovered unchanged.

Malic Acid Polymer (Product A)

The acid mixture was adequate, however, for the nitration of this water-soluble polycondensate. A three molar excess of acid was found to be sufficient. The product, (I), was obtained upon pouring the reaction mixture into a large excess of acetone. Water was ineffective.

The white flocculent precipitate decomposed instantly to a brown oil when exposed to the air in the presence of acid, and hence was washed very carefully with a slightly alkaline water-acetone mixture in an attempt to remove the last traces of acid. This was successful temporarily, and a white amorphous solid was isolated, but the material invariably decomposed while air-drying after about forty-eight hours. In view of this, further investigation of this compound was abahdoned.

Nitrations with Fuming Acid and Acetic Anhydride

The succinic acid polymer (Pruduct B):

The nitration of this polymer seemed successfully to be done with the fuming nitric acid - acetic anhydrate mixture, (acetyl nitrate). The yield was quantitative. Considerable swelling of the powdered solid prior to solution was observed on initial contact with the nitration mixture. This property is generally characteristic of high polymers.

A white, flocculent precipitate was obtained on pouring the reaction mixture into a large excess of water. On extensive washing by decantation, the material tended to coagulate and settle. When no trace of acid remained, filtration and air-drying yielded a white amorphous solid (IV).

Anal. Calcd. for $C_6H_8O_6N_4$(see discussion): N, 24.15
Found 23.47, 23.60.

The compound was instantly and irreversibly soluble, with some discoloration - apparently decomposed - in dilute aqueous alkali. On treatment with liquid acetone, IV was changed instantaneously to the familiar brown semi-solid (V) and dissolved rapidly in the acetone. On the addition of water, V was reprecipitated as a light-coloured gum. Other common organic solvents, i.e., ether, benzene, methanol, ethanol, carbon disulfide, carbon tetrachloride, and chloroform, had no effect, including no solvent action.

The thermal behaviour of IV is also very interesting. When heated slowly in air, it changed at 60° into a material later identified as V above. On further heating, it started to decompose rapidly at 81°, with the evolution of large quantities of gas (second stage). However, when the original material was immersed in water, and the temperature raised slowly to 100°, no decomposition of any kind took place. This was also the case with various organic solvents at their boiling points. There were signs that melting had taken place, but the precise melting point was difficult to determine under these conditions. The compound thus seems to have no inherent thermal instability, but to be readily attacked by oxygen at elevated temperatures.

When samples were inadequately washed after nitration (less than five liters of water per gram), and confined in a closed container, they changed spontaneously to the primary decomposition product V within twenty-four hours. Similar samples left open to the air required more time, about seven days. In general, small grains seemed more stable than large lumps. Lumps left to air-dry overnight were found frequently to have streaks of brown material along sharp edges and protuberances - an interesting confirmation of the physical law that the vapour pressure of a liquid is greatest where the radius of curvature is least. The water, evaporating chiefly at those sharp edges, would tend to carry any residual decomposition-causing nitric acid with it, and deposit it at its place of exit. Of course, any discoloured material was always removed from any sample before further testing.

When thoroughly air-dried, IV burned very vigorously-virtually instantaneously - leaving a small residue. It reacted explosively with concentrated sulfuric acid. When tested at Explosives Laboratory, Natural Research Council, Ottawa, it was found to have a sensitivity coefficient of 32 (81), i.e., in ratio approximately three times more sensitive to impact detonation than T.N.T.

The primary decomposition product V was shown to be identical with the materials produced from IV thermally and autocatalytically, by secondary decomposition point determinations. It was strongly odoriferous (although the original material also had a fairly distinct acetic acid-like odour, possibly due to traces of V). It burned quite vigorously. It was completely insoluble in cold water and organic solvents except acetone, but seemed slightly soluble in boiling water and gave a strongly acid reaction.

On standing, V tended to assume a putty-like consistency. After heating at 110°, the residue was a water-soluble brown oil (VI). Heating at 125° in air resulted in complete charring, with the liberation of large volumes of gas.

The malic acid polymer (Product A)

On treating the polycondensate with the mixed reagents a material was obtained which was probably the fully nitrated compound (II). The yield was quantitative.

In physical appearance II resembled I, but was precipitated from an excess of water rather than of acetone. It was thoroughly washed with water by decantation.

II was very rapidly soluble in aqueous alkali, with some discoloration, and this was completely nonreversible - indicating probable decomposition. It was instantaneously decomposed to a brown gum by acetone. Like I, II could be isolated as a white amorphous powder, but despite all precautions, persistently changed to a brown semi-solid before it could be dried sufficiently for analysis.

III had a slight odour of acetic acid, was water insoluble, and when shaken with water gave a slightly acid reaction. On heating II in air to 58°, III was obtained (stage 1 decomposition). SUbsequent heating resulted in the decomposition of III at about 78° (stage 2 decomposition), with the evolution of large quantities of unidentified gas.

Nitration of certain salts:

As a side experiment, the nitration of the succinic acid - ethylene diamine salt was attempted under conditions identical with those used above. No product was obtained upon pouring the nitration mixture into water or any other organic solvent. A similar result was obtained with the malic acid salt under the same conditions.

Malic acid polymer (Product B)

This compound was stirred with acetyl nitrate for twenty hours, but was found to be almost completely insoluble. It was recovered unchanged.

Tartaric acid polymer (Product B)

The attempted nitration likewise failed here after lengthy stirring, and the starting material was recovered unchanged.

DISCUSSION OF RESULTS - NITRATION OF POLYAMIDES

Nitrations with Concentrated Nitric Acid and Acetic Anhydride

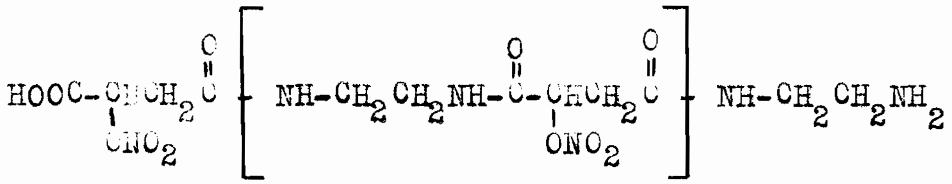
This reagent was used for theoretical purposes, in an attempt to obtain partial nitration.

The succinic acid polymer (Product A):

Evidently, this nitrating agent was not capable of substituting the nitrogen-bonded hydrogen atoms of the polyamide for nitro groups.

The malic acid polymer (Product A):

As the nitrogen-bonded hydrogen atoms of the succinic acid polymer were not attacked under the identical conditions it is unlikely that here they have been substituted. It is highly probably that only the hydroxy groups of this polymer have been nitrated. The expected structure of the product is then



$$HOOC-\underset{ONO_2}{CH}CH_2\overset{O}{\overset{\|}{C}}\left[NH-CH_2CH_2NH-\overset{O}{\overset{\|}{C}}-\underset{ONO_2}{CH}CH_2\overset{O}{\overset{\|}{C}}\right]NH-CH_2CH_2NH_2$$

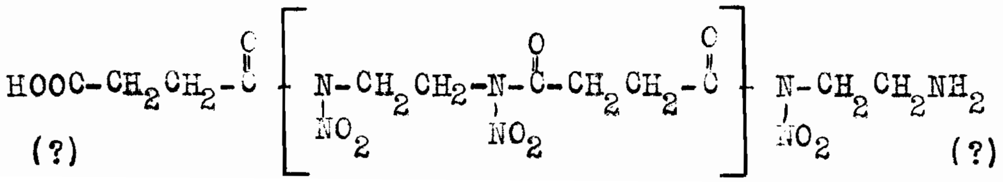
where "n" probably lies between three and five.

The instability of this substance tends to confirm the generally accepted fact that compounds with hydroxyl groups adjacent to carbonyl groups give unstable nitrates.

Nitrations with Fuming Nitric Acid and Acetic Anhydride

The succinic acid polymer (Product B)

Evidently, nitration has successfully been effected here. The expected structure of the product IV is



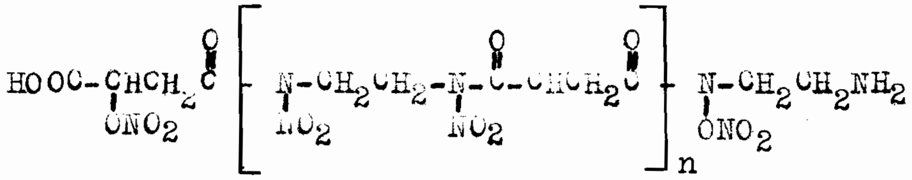
$$\underset{(?)}{HOOC}-CH_2CH_2-\overset{O}{\overset{\|}{C}}\left[\underset{NO_2}{N}-CH_2CH_2-\underset{NO_2}{N}-\overset{O}{\overset{\|}{C}}-CH_2CH_2-\overset{O}{\overset{\|}{C}}\right]\underset{NO_2}{N}-CH_2CH_2\underset{(?)}{NH_2}$$

Here "n" may be 10 to 25 to correspond with a molecular weight of 2000 to 5000.

It is possible only to speculate regarding the nature of the primary decomposition product, V. Due to the difficulty of purification and drying, no analysis was attempted. The fact that burning was quite vigorous indicates that an appreciable number of nitramine ($-N-NO_2$) groups still remain. The gum-like texture of V, plus the well-known stability of polyamide chains, militates against the possibility that extensive chain degredation has occurred. The acidity of the hot aqueous extract suggests the liberation of acid-forming substances, such as the oxides of nitrogen. Finally, the easy solubility in water of the subsequent decomposition product VI suggests the presence of many hydroxy groups in VI and implies the possibility of some in V. Thus V may be essentially undegraded IV, with some of the nitro groups replaced by hydroxyl.

The malic acid polymer (Product A)

In view of the fact that the succinic acid polymer has successfully been nitrated, and in view of the differences in properties between this product and that of the suggested partial nitration, it is virtually certain that the completely nitrated malic acid low polymer has been obtained. The structure, then, is

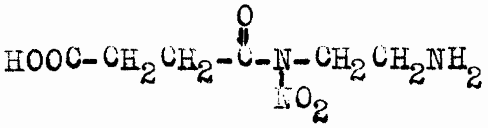


$$\mathrm{HOOC{-}\underset{ONO_2}{C}HCH_2\overset{O}{\overset{\|}{C}}\left[-\underset{NO_2}{N}{-}CH_2CH_2{-}\underset{NO_2}{N}{-}\overset{O}{\overset{\|}{C}}{-}CHCH_2\overset{O}{\overset{\|}{C}}-\right]_n\underset{ONO_2}{N}{-}CH_2CH_2NH_2}$$

where "n" is probably 3 to 5, on the assumption that no degradation has taken place.

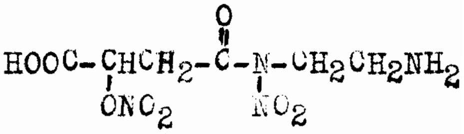
Attempted nitration of the salts:

In view of the successful nitration of the corresponding polymers under the same conditions, it is highly probable that nitration of the salts has taken place, to yield the compounds



$$\mathrm{HOOC{-}CH_2CH_2{-}\overset{O}{\overset{\|}{C}}{-}\underset{NO_2}{N}{-}CH_2CH_2NH_2}$$

and



$$\mathrm{HOOC{-}\underset{ONO_2}{C}HCH_2{-}\overset{O}{\overset{\|}{C}}{-}\underset{NO_2}{N}{-}CH_2CH_2NH_2}$$

but that none of the precipitating agents used was adequate.

In any event, this tends to indicate that no extensive degradation has occurred during nitration of the polymer, as this would be bound to produce some water-soluble monomeric nitramine.

The malic acid polymer (Product B):

The complete insolubility of this substance in the mixture of fuming nitric acid and acetic anhydride tends strongly to verify the highly cross-linked structure suggested for it.

The tartaric acid polymer (Product B):

The failure of the attempted nitration here likewise confirms the hypothesis regarding the structure of this polymer.

SUMMARY

The results of the experimental work of this investigation should first be reviewed in reference to the original purpose of the work. It had been decided to attempt to synthesize certain nitrated polyamides for potential use as explosives. These polyamides were to be formed from ethylene diamine and succinic acid, and from the hydroxyl group substituted malic and tartaric acids. Subsequently, it had been decided by this investigator to carry out the polyamide preparations by two methods, one drastic and the other relatively mild; one tending to lead to low molecular weight products, and the other to the highest molecular weights obtainable by ordinary means. This was as a matter of theoretical interest, and also in order to determine optimum conditions. For the same reason, the nitrations were carried out with two mixtures of differing potency.

It was found that the polymerization of succinic acid with ethylene diamine resulted, for all practical purposes, in identical products with both methods of preparation. The polymer could be nitrated under appropriate conditions. The product of the nitration was chemically stable, but was quite easily decomposed, apparently without degredation, in the presence of traces of acid. It was definitely an explosive, and of the initiator class, but a thorough and time-consuming

investigation of its behaviour as an explosive has yet to be made. However, this substance has one characteristic that almost certainly will prevent its practical use as an explosive: that is, its thermal instability. It decomposes at about 60°, and ordinary explosives must be stable at temperatures at least as high as 80°. Moreover, none of the other nitrated polymers that were prepared show any promise. It must be concluded, then, that while the compounds whose synthesis had been planned had, in general, succesfully been prepared, they nevertheless were not suitable for use as practical explosives. This, incidentally, is also the conclusion arrived at after the majority of investigations into the preparation of explosive polymers, and in particular in the departmental research project of which this work was a part.

From a theoretical point of view, however, the investigation was of considerable interest. The results are quite decisive and easily interpreted; moreover, they tend to confirm some of the specific assumptions that of necessity have had to be made in the course of this thesis.

The nitration of polymeric amides was undertaken in an attempt to combine the known stability of linear polyamide chains with the high explosive power of nitrated amide linkages. A succinic acid - ethylene diamine polymer was synthesized, nitrated, and was found to be both reasonably stable as a chemical compound, and also active as an explosive. Unfortunately, the increase in stability due to chain formation was not sufficient to permit of practical use of the substance under the rigorous conditions of modern warfare.

Under mild conditions, a material was synthesized which, it was suggested without decisive proof, was a low molecular weight polymer of malic acid and ethylene diamine. It would be expected that, when nitrated, this substance would be intermediate in stability between the relatively highly polymeric nitramides, and the very easily hydrolyzed nitrated amides. This was found to be the case.

Under drastic conditions, materials were obtained which, it was suggested, likewise without decisive proof, were highly cross-linked polymers of malic and tartaric acids with ethylene diamine. It would be expected that these would be greatly resistant to nitration. This was also found to be the case.

The difficulty of sythesizing normal polymers of hydroxy acids with amines is clearly indicated. Mild reaction conditions lead to unsatisfactory low molecular weight products. Drastic conditions lead equally unsatisfactorily to extensive cross-linking. It is certain that, in order to prepare linear polyamides of adequate molecular weight from hydroxy dicarboxylic acids, a thorough investigation of optimum conditions will have to be made.

In conclusion, an interesting program of future research can be drawn up, on the basis of these findings. The relation between degree of polymerization and ease of decomposition of nitrated polyamides can be further investigated, as can other methods and other conditions for the preparation of hydroxy-substituted polyamides. It is to hoped that light will some day be cast on these questions.

LIST OF REFERENCES

1. Simon, Ann. 31, 265 (1839)
2. Baeyer, Ber. 5, 25, 280, 1094 (1872)
3. Baekeland, L., J. Ind. Chem. 1, 159 (1909)
4. Wheeler and Jackson, J. Amer. Chem. Soc. 24, 752 (1902)
5. Stephen Short, & Gladding, Chem. Soc. Trans. 117, 513 (1920)
6. Holzer, Ber. 17, 659 (1889)
   Ludy, Wien. Akad. Ber. 118, 191 (1889)
7. Beetle Prods. Co., U.S. Pat. 248, 477 (1926)
8. U.S. Pat. G.P. 392, 090 (1917). G.P. 394,217 (1926)
9. R.L. Brown, J. Ind. Eng. Chem. (1925)
10. F. Malthus, Treatise of Artificial Fireworks (1629)
11. Bate, John, The Mysteries of Nature & Art, London, (1635)
12. Nobel, Alfred, English patent 1,345 (1867)
13. Sprengel, English patent 2,642 (1871)
    ibid J. Chem. Soc. p. 796 (1873)
14. Turpin, E., French Patent 167,512 (1885)
    German patent 38, 734 (1886)
15. Kneitsch, Ber. 190, 4093 (1901); Chem. Ind. p.6, (1902)
16. Colver, High Explosives, London Tech. Press (1938)

17.- 39.- Deleted

40. Davis, Chem. of Powd. & Explosives, Vol. 1, 189 (1941)

41. Marshall, Explosives, Vol. 1, 377-387
42. Robertson, R., Trans. Chem. Soc. 119, 13, (1921)
43. Marshall, Explosives, Vol. 2, 208-212
44. Private Communication, Dr. I.R. McHaffie, Canadian Industries Limited
45. W.H. Carothers & G.J. Berchet, J. Am. Chem. Soc. 52, 5289-5291 (1930)
46. W.H. Carothers & J.W. Hill, J. Am. Chem. Soc. 54, 1557-1559 (1932)
47. W.H. Carothers & J.W. Hill, J. Am. Chem. Soc. 54, 1566-1569 (1932)
48. W.H. Carothers, U.S. Pat. 548, 701 (1931)
49. ibid U.S. Pat. 2,071,253 (1937)
50. ibid U.S. Pat. 2,130,523 (1938)
51. Ber. 20, 1445,(1887)
52. Ber. 27, R, 404 (1894)
53. W.H. Carothers, U.S. Pat. 2,130,947 (1937)
54. ibid U.S. Pat. 2,130,948 (1937)
55. W.O. Baker & C.S. Fuller, J. Am. Chem. Soc. 64, 2399 (1942)
56. W.O. Baker & C.S. Fuller, J. Am. Chem. Soc. 65, 1120 (1943)
57. K. Hess & H. Kiessig, Naturwissenchaften 31, 171 (1943) (see Mark & Proskauer, Resins, Rubbers, Plastics C-2: 112.1)
58. H. Staudinger & H. Jorder, J. Prakt. Chem. 160, 178-194 (1943) (see Mark & Prosk. C-2:163)

LIST OF REFERENCES

1. Simon, Ann. 31, 265 (1839)

2. Baeyer, Ber. 5, 25, 280, 1094 (1872)

3. Baekeland, L., J. Ind. Chem. 1, 159 (1909)

4. Wheeler and Jackson, J. Amer. Chem. Soc. 24, 752 (1902)

5. Stephen Short, & Gladding, Chem. Soc. Trans. 117, 513 (1920)

6. Holzer, Ber. 17, 659 (1889)
   Ludy, Wien. Akad. Ber. 118, 191 (1889)

7. Beetle Prods. Co., U.S. Pat. 248, 477 (1926)

8. U.S. Pat. G.P. 392, 090 (1917). G.P. 394,217 (1926)

9. R.L. Brown, J. Ind. Eng. Chem. (1925)

10. F. Malthus, Treatise of Artificial Fireworks (1629)

11. Bate, John, The Mysteries of Nature & Art, London, (1635)

12. Nobel, Alfred, English patent 1,345 (1867)

13. Sprengel, English patent 2,642 (1871)
    ibid J. Chem. Soc. p. 796 (1873)

14. Turpin, E., French Patent 167,512 (1885)
    German patent 38, 734 (1886)

15. Kneitsch, Ber. 190, 4093 (1901); Chem. Ind. p.6, (1902)

16. Colver, High Explosives, London Tech. Press (1938)

17.- 39.- Deleted

40. Davis, Chem. of Powd. & Explosives, Vol. 1, 189 (1941)

59. A. Matthes, J. Prakt. Chem. 162, 245 (1943) (see Mark & Proskauer C-2:163)

60. Staudinger, Frey & Starck, Ber. 60, 1782 (1927)

61. Staudinger & Schwalbach, Ann. 488 (1931)

62. H.W. Matheson & F.W. Skirrow, U.S. Pat. 1,752,362 (1929)

63. W. Smith, J. Soc. Chem. Ind. 20, 1075 (1901)

64. E. Linnemann, Ann. 163,369 (1872)

65. Proceedings of the Polymer Subcommittee of the Associate Committee on Explosives , National Research Council. Minutes of the Sixth Meeting, Dec. 16, 1944. Also Private Communication, D.M. MacLean.

66. Eighth Meeting as above, Feb. 24, 1945. Also Private Communication, D.M. MacLean

67. Private Communication, Mrs. J. Musgrave

68. Polymer Subcommittee (see ref. 65),Ninth meeting

69. ibid Seventh meeting

70. United States O.S.R.D. interim reports, Preparation and Testing of Explosives." Dec. 15, 1942 to Jan. 15, 1944. "Preparation of Polymers which may be of Interest as Explosives."

71. ibid Dec. 15, 1942

72. ibid Feb. 15, 1943

73. ibid Feb. 15, 1943

74. ibid June 15, 1943

75. United States O.S.R.D. reports as per ref. 70, July 15, 1943

76. ibid August 15, 1943

77. ibid Sept. 15, 1943

78. ibid Jan. 15, 1944

79. ibid April 15, 1943

80. Private Communication, G. Bowen

81. Private Communication, M.C. Fletcher

82. H.S. Hill & H. Hibbert, J. Am. Chem. Soc. 45, 3108, 3117 (1923)

83. Baumann, Ann. 163, 308 (1872)

84. Ber. 27, R, 404 (1894)

85. Polymer Subcommittee, cf. ref. 65, Third Meeting, p.4

86. ibid Third Meeting, p.3