[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

Polymers of α-Acetamidoacrylic Acid and its Methyl Ester

BY ROGER ADAMS, JAMES L. JOHNSON AND BRUCE ENGLUND[1]

The polymerization of α-acetamidoacrylic acid was accomplished by heating a concentrated aqueous ammonia solution of the monomer in presence of a trace of ascaridole. The use of ultraviolet light, benzoyl peroxide, or of a reduction–activation system of ammonium persulfate, sodium metabisulfite and cupric sulfate in water or ethanol failed. However, 2,2′-bis-azo-isobutyronitrile as catalyst readily caused polymerization of α-acetamidoacrylic acid in ethanolic solution yielding a very water-soluble, infusible polymer similar to that obtained in aqueous ammonia.

Attempts to hydrolyze by 15% aqueous ethanolic alkali in order to deacetylate the polymer failed and by the action of 40% aqueous alkali a product, which could not be purified, resulted. Hydrolysis by means of aqueous hydrochloric acid also gave unsatisfactory results. The hydrolyzed product was obviously not an amino acid polymer for it did not give more than a slight ninhydrin test and showed practically no primary amino nitrogen. It probably contains lactam groupings, as the analyses were several per cent. high in carbon for the simple amino acid polymer but not correct for uniform lactamization.

The direct esterification of α-acetamidoacrylic acid was attempted and failed, due to decomposition of the acid in the presence of mineral acids, though this method of preparation of esters is reported in a patent.[2] Two molecules of diazomethane react with α-acetamidoacrylic acid to form the methyl ester of 3-acetamidopyrazoline-3-carboxylic acid. Because α,α-diacetamidopropionic acid is so readily converted to α-acetamidoacrylic acid,[3] the analogous reaction was attempted with methyl α,α-diacetamidopropionate, but it was found that this ester does not eliminate acetamide. Moreover, acetamide could not be added to methyl pyruvate under the conditions used for the preparation of α,α-diacetamidopropionic acid. Methyl α-acetamidoacrylate was successfully prepared, however, by the action of methyl iodide on silver α-acetamidoacrylate, a method identical with that recently described by Rothstein.[4]

Methyl α-acetamidoacrylate polymerizes merely on standing for some time at room temperature, provided inhibitors are not present. Heating the monomer in the presence of benzoyl peroxide as a catalyst converts it to polymer. Gudgeon[2] reported the polymerization of this ester by heating in presence of benzoyl peroxide or by heating in aqueous solution with the same catalyst. He describes his products as clear, hard, colorless resins which agree with the properties obtained in this investigation.

Most interesting was the observation that the methyl α-acetamidoacrylate polymer may be obtained in an anhydrous form or as a stable hydrated form containing one-half molecule of water per monomer unit. The hydrated form results when polymerization is effected in solvents containing water or when the anhydrous form is reprecipitated from such solutions.

The anhydrous polymers began to soften above 135° and melted to a clear liquid at 200–220°, with decomposition at temperatures above 220°. On the other hand, the hydrated form was infusible, decomposing when heated at 320–355° with only slight previous sintering above 285°. The anhydrous polymers were of relatively low molecular weight $[\eta] = 0.127$ and 0.162 while the polymers prepared as hydrates were of higher molecular weight $[\eta] = 2.32$ and 5.75. When an anhydrous polymer fraction, m. p. 200–220°, with intrinsic viscosity $[\eta] = 0.127$ was hydrated, the product sintered slightly at 235–285°, decomposed without liquefaction at 320–345° and had an intrinsic viscosity $[\eta] = 0.149$.

The infrared spectra of the anhydrous and hydrated forms showed no characteristic differences. X-Ray diffraction patterns did not reveal significant differences in the products.

Copolymers of α-acetamidoacrylic acid and acrylonitrile were formed when ethanolic or aqueous solutions of monomer mixtures were heated with benzoyl peroxide, 2,2′-bis-azo-isobutyronitrile, or ammonium persulfate–sodium metabisulfite as catalysts. These had physical properties very similar to those of polyacrylonitrile. Even a copolymer of average composition 61% α-acetamidoacrylic acid and 39% acrylonitrile was very water-insoluble. All the copolymers were infusible, decomposing when heated at 300–350°. A copolymer, of average composition 95% acrylonitrile and 5% α-acetamidoacrylic acid having an intrinsic viscosity $[\eta] = 2.92$, was prepared and found to possess fiber- and film-forming properties. The infrared spectrum of one of these copolymers was determined and showed the presence of monosubstituted amide and carboxylic acid groups as well as cyano groups.

Experimental

Poly-α-acetamidoacrylic Acid. (A).—A solution of 5 g. of α-acetamidoacrylic acid in 50 ml. of 29% aqueous ammonia was heated under reflux on a steam-bath for two hours in presence of one drop of ascaridole. The heating was continued while the ammonia and water were evaporated by a stream of air. The yellow residue (gummy if still moist but otherwise brittle) was dissolved in 40 ml. of water, the solution filtered, and 5 ml. of concd. aqueous

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(1) Atomic Energy Commission Predoctoral Fellow, 1949–1950.

(2) Gudgeon, British Patent 577,771, May 30, 1946; U. S. Patent 2,461,383, Feb. 8, 1949.

(3) Bergmann and Grafe, *Z. physiol. Chem.*, **187**, 187 (1930).

(4) Rothstein, *J. Chem. Soc.*, 1968 (1949).

hydrochloric acid was added to the filtrate. Precipitation of the polymer was effected by adding slowly 350 ml. of 95% ethanol to the acidified solution. The polymer was separated by centrifuging and washed in the centrifuge bottle several times with ethanol, acetone, and ether. The product, which was dried in a vacuum desiccator, was a powdery white material weighing 3.5 g. (70%). It decomposed without melting at 320–350° and absorbed moisture in the air. It was soluble in water, slightly soluble in methanol and 95% ethanol, insoluble in absolute ethanol, *m*-cresol, and dimethylformamide. The sample for analysis was dried at 100° for thirty-six hours at 1-mm. pressure over phosphorus pentoxide.

Anal. Calcd. for $C_5H_7O_3N$: C, 46.52; H, 5.47; N, 10.81. Found: C, 46.25; H, 5.53; N, 10.87.

This product (0.11 g. in 20 ml. of water at 28°) had an intrinsic viscosity $[\eta] = 0.71$. By diluting 5 ml. of the above solution to 10 ml. with water $[\eta] = 1.08$.

(B).—A solution of 3.0 g. of α-acetamidoacrylic acid in 65 ml. of 95% ethanol was heated to reflux, and 0.10 g. of 2,2′-bis-azo-isobutyronitrile was added. Within five minutes a precipitate appeared. The reaction mixture was kept at reflux for five hours. The precipitated polymer was separated by filtration, washed with ethanol and dried. The yield of poly-α-acetamidoacrylic acid was 1.3 g. The filtrate yielded 1.1 g. of monomer. The polymer decomposed without melting when heated to 310–335° (uncor.) and had an intrinsic viscosity $[\eta] = 0.198$.

Anal. Calcd. for $C_5H_7NO_3$: C, 46.52; H, 5.47. Found: C, 46.69; H, 5.77.

Irradiation with ultraviolet light for forty-eight hours of the monomer in ammoniacal solution in presence of ascaridole did not cause polymerization. Use of benzoyl peroxide in aqueous ammonia in place of ascaridole was ineffective in inducing polymerization.

Hydrolysis with Hydrochloric Acid.—A solution of 3.7 g. of poly-α-acetamidoacrylic acid in 30 ml. of water and 30 ml. of concd. aqueous hydrochloric acid was refluxed on a steam-bath for three hours. After twenty minutes a white gel had formed. After dilution with 150 ml. of ethanol, the solid was separated by centrifuging and washed with ethanol and acetone. After drying, the slightly yellowish product weighed 2.25 g., decomposition point 320–340°. Traces of halogen were removed by a treatment with pyridine at room temperature after which it was white.

The product is soluble in 10% aqueous sodium hydroxide. It is soluble in concd. sulfuric acid from which it is recovered unchanged by dilution with water. It is insoluble in water, aqueous ammonia, glacial acetic acid, pyridine, methanol, ethanol, *m*-cresol or dimethylformamide.

Anal. Calcd. for $C_3H_5O_2N$ (polyaminoacrylic acid): C, 41.37; H, 5.79. Found: C, 50.54; H, 4.98.

3-Acetamidopyrazoline-3-carboxylic Acid Amide.—To the ether solution of diazomethane prepared from 3 g. of N-nitrosomethylurea was added 2 g. of α-acetamidoacrylic acid. Nitrogen was evolved and part of the solid went into solution. The mixture was allowed to stand overnight then filtered to remove 0.8 g. of unreacted α-acetamidoacrylic acid. After removal of the ether a yellow oil remained. This was dissolved in a mixture of 2 ml. of ethanol and 2 ml. of concentrated aqueous ammonia. The water, ethanol and ammonia were removed in an air stream and the residue crystallized from methanol, m. p. 183.5–185° (cor.).

Anal. Calcd. for $C_6H_{10}O_2N_4$: C, 42.10; H, 6.48. Found: C, 42.17; H, 6.22.

Poly Methyl α-Acetamidoacrylate (Hydrate).—A solution of 0.9 g. of methyl α-acetamidoacrylate[4] in 100 ml. of ordinary benzene was refluxed with 2.5 mg. of benzoyl peroxide. After nine hours an additional 2.5 mg. of benzoyl peroxide was added and reflux continued for a total of twenty-three hours. The solvent was evaporated and the residue washed with ether. The yield of polymer was 0.7 g. It sintered when heated above 310° and decomposed at 335–355° (uncor.). It had an intrinsic viscosity $[\eta] = 2.32$. The sample for analysis was reprecipitated from methanol solution with ordinary ether.

Anal. Calcd. for $C_6H_9NO_3 \cdot 0.5H_2O$: C, 47.35; H, 6.63. Found: C, 47.30; H, 6.60.

Polymeric methyl α-acetamidoacrylate obtained as a by-product from the preparation of the monomer was similarly purified and was shown by analysis to be a hydrate of the same composition as above. Heating the hydrate at 180° for twenty-seven hours above phosphorus pentoxide at 0.5 mm. pressure effected no change.

Poly Methyl α-Acetamidoacrylate (Anhydrous).—A solution of 2.0 g. of methyl α-acetamidoacrylate and 3.0 mg. benzoyl peroxide in 100 ml. of dry benzene was heated to reflux. After twelve hours, 2.0 mg. of benzoyl peroxide was added, and after fourteen hours, 10 mg. more was added. After sixteen hours monomer was still present (the solution decolorized bromine). The solvent was evaporated off at reduced pressure to 20 ml. volume, causing some solid to separate. The addition of 20 ml. of dry petroleum ether (b. p. 40–60°) produced an abundant, white, powdery precipitate of poly methyl α-acetamidoacrylate, which weighed 1.0 g. after being thoroughly washed with petroleum ether; 0.5 g. of monomer was recovered from the washings.

The anhydrous polymer softens when heated above 135°, is a translucent semi-solid at 185°, and melts to a clear, colorless, mobile liquid at 205–215° (cor.), decomposing when heated further.

Anal. Calcd. for $C_6H_9NO_3$: C, 50.34; H, 6.34. Found: C, 50.48; H, 6.53.

This polymer had an intrinsic viscosity $[\eta] = 0.162$. A similar procedure using 2,2′-bis-azo-isobutyronitrile as catalyst gave a polymer of similar melting point with intrinsic viscosity $[\eta] = 0.127$.

Hydration of Poly Methyl α-Acetamidoacrylate (Anhydrous).—A 200-mg. sample of anhydrous poly methyl α-acetamidoacrylate, melting at 205–215° and having an intrinsic viscosity $[\eta] = 0.127$, was dissolved in 5.0 ml. of water and boiled with the addition of three 20-ml. portions of acetone until the remaining volume was 5 ml. The cloudy solution precipitated a gum when cooled, which was separated and dried in a vacuum desiccator to a white powder. The product thus obtained decomposed without melting at 320–345° (uncor.), after slight previous sintering above 235°. The intrinsic viscosity was $[\eta] = 0.149$.

Copolymerization of Acrylonitrile and α-Acetamidoacrylic Acid.—Catalyst solutions were prepared by dissolving 1.46 g. of ammonium persulfate in 20 ml. of water, and 0.37 g. of sodium metabisulfite in 10 ml. of water.

A solution of 14.25 g. of acrylonitrile and 0.75 g. of α-acetamidoacrylic acid in 125 ml. of water was heated to 70°, and 1 ml. of each of the above catalyst solutions was added. Precipitation of polymer began almost at once, and the temperature rose to 85°. After ten minutes the solution was filled with a thick, spongy, white precipitate which was separated by filtration, washed with ethanol and ether and dried. The yield was 11.25 g. (75%).

Anal. Calcd. for 95% C_3H_3N + 5% $C_5H_7NO_3$: C, 66.83; H, 5.96. Found: C, 66.78; H, 5.73.

The copolymer began to turn yellow above 210°, and decomposed without melting at 305–350°. The intrinsic viscosity was $[\eta] = 2.92$.

Summary

1. α-Acetamidoacrylic acid is polymerized in aqueous ammonia when catalyzed by ascaridole or in ethanol when catalyzed by 2,2′-bis-azo-isobutyronitrile.

2. Methyl α-acetamidoacrylate polymerizes slowly on standing but rapidly in presence of peroxide catalysts. An anhydrous form is produced when anhydrous conditions are used. A hydrated form results if a solvent containing water is employed or when the anhydrous form is reprecipi-

tated from such solutions. It contains a half molecule of water per monomer unit which cannot be removed by long heating *in vacuo*.

3. α-Acetamidoacrylic acid may be copolymerized with acrylonitrile.

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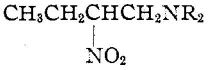
Alkylation of Nitroparaffins with Amines and Their Derivatives

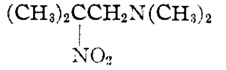
BY H. R. SNYDER AND WILLIAM E. HAMLIN

Certain amines have been employed in the alkylation of simple nitroparaffins[1,2,3] and nitro esters[4] but no general procedure for carbon-alkylation of nitroparaffins by amines has been developed as yet. It seems possible that the amines employed, which are Mannich bases, may serve as sources of unsaturated compounds and that the apparent alkylations are actually condensations of the Michael type. This consideration suggests that the Mannich bases of 1-nitropropane (I), which can undergo the elimination of secondary amine, might be used in the alkylation of other nitroparaffins, whereas the Mannich bases of 2-nitropropane (II) should be inert. It was found that 1-nitropropane and 2-nitropropane were alkylated by the Mannich bases (Ia and Ib) to yield 3,5-dinitroheptane (IIIa) and 2-methyl-2,4-dinitrohexane (IIIb),[5] respectively. Apparently the use of a basic catalyst is not necessary in the alkylation of 1-nitropropane and, in fact, may increase the decomposition of the Mannich base. It was found that N-(2-nitrobutyl)-dimethylamine (Ia), which was prepared in the course of this investigation, is more stable in storage than the corresponding diethylamine (Ib).



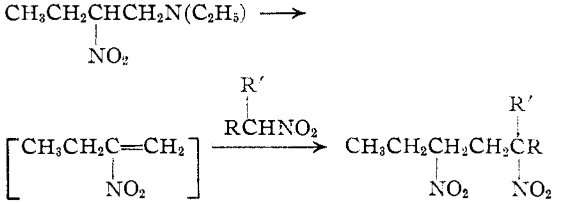
$CH_3CH_2\underset{NO_2}{CH}CH_2NR_2$

I, R = (a) CH_3 (b) C_2H_5



$(CH_3)_2\underset{NO_2}{C}CH_2N(CH_3)_2$

II

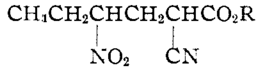


$$CH_3CH_2\underset{NO_2}{CH}CH_2N(C_2H_5) \longrightarrow \left[CH_3CH_2\underset{NO_2}{C}{=}CH_2\right] \xrightarrow{R\overset{R'}{C}HNO_2} CH_3CH_2\underset{NO_2}{CH_2}CH_2\underset{NO_2}{\overset{R'}{C}}R$$

III, (a) R = C_2H_5, R′ = H
(b) R = R′ = CH_3

3,5-Dinitroheptane was catalytically reduced to 3,5-diaminoheptane and a benzenesulfonamide derivative was prepared. Application of the Nef reaction to the dinitro compound yielded a very small amount of 3,5-heptanedione which was identified as its copper salt. Catalytic reduction of 2-methyl-2,4-dinitrohexane yielded the corresponding diamino compound from which a phenylthiourea derivative was prepared.

The Mannich base of 1-nitropropane (Ib) was also found to alkylate ethyl and methyl cyanoacetate to yield the corresponding α-cyano-γ-nitrocaproates (IV), but resinification was considerable. The use of sodium hydroxide catalyst was found to be undesirable. Ethyl α-cyano-γ-nitrocaproate has been prepared previously from 2-nitro-1-butene and cyanoacetic ester.[6]



$CH_3CH_2\underset{NO_2}{CH}CH_2\underset{CN}{CH}CO_2R$

IV, R = (a) C_2H_5, (b) CH_3

It would be expected that an amine exchange reaction similar to those of ketonic Mannich bases[7] could also occur with the Mannich base of 1-nitropropane. Actually, N-(2-nitrobutyl)-piperidine was obtained along with resinous material when N-(2-nitrobutyl)-dimethylamine (Ia) was refluxed with excess piperidine.

The quaternary ammonium salt formed by the addition of methyl iodide to the Mannich base of 1-nitropropane would also be expected to be a good alkylating agent. Unfortunately, all attempts to prepare this salt failed, apparently because it decomposed in the presence of methyl iodide; the reaction mixtures had the odor and lachrymatory property of 2-nitro-1-butene.

The Mannich base of 2-nitropropane, N-(2-nitroisobutyl)-dimethylamine (II), is not structurally capable of producing an unsaturated intermediate which is considered necessary for condensation with nitroparaffins. The assumed unreactivity was tested by heating the amine (II) with excess 2-nitropropane in the presence of sodium hydroxide. There was no evidence of reaction. An amine exchange reaction with piperidine also failed.

Recently the acid catalyzed amine exchange reaction of 1-methylgramine with piperidine was reported.[8] N-(2-Nitroisobutyl)-dimethylamine

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(1) Reichert and Posemann, *Arch. Pharm.*, **275**, 67 (1937).

(2) Snyder and Katz, THIS JOURNAL, **69**, 3140 (1947).

(3) Snyder and Pellegrini, unpublished work.

(4) Weisblat and Lyttle, THIS JOURNAL, **71**, 3079 (1949); **69**, 2118 (1947).

(5) Since the completion of this work Bahner and Kite have reported the synthesis of these two compounds by addition of 1-nitropropane and 2-nitropropane to 2-nitro-1-butene (THIS JOURNAL, **71**, 3597 (1949)); in that report the second compound is erroneously named as 3,5-dinitro-3-methylhexane.

(6) Bahner, U. S. Patent 2,426,158 [*C. A.*, **41**, 7410 (1947)].

(7) Snyder and Brewster, THIS JOURNAL, **70**, 4231 (1948).

(8) Snyder and Eliel, *ibid.*, **70**, 4233 (1948).