DPN, following one and one-half hours exposure in the ultraviolet apparatus employed, showed an 18% decrease in 340 mμ absorption when assayed by the hydrosulfite method described by Lepage.[2] The data in Fig. 3 indicate that the spectral changes in solutions of DPN exposed to ultraviolet radiation are to a large extent accounted for by reactions of the nicotinamide moiety of the molecule. Component no. 1 (Fig. 2), which exhibits the nicotinamide spectrum and a white fluorescence, is probably a photochemically altered pyridinium compound split from the DPN molecule whereas component no. 3, which has the absorption spectrum of DPN, is believed to be DPN with a photochemically altered nicotinamide moiety.

Ultraviolet radiation of solutions of DPN did not liberate inorganic phosphorus from the molecule, whereas in the experiment illustrated in Fig. 1, 10 μg. of inorganic phosphorus per mg. of ATP was formed in the course of a six-hour exposure to ultraviolet radiation.

Discussion

The above data indicate that several reactions take place in the decomposition of DPN by ultraviolet radiation including photochemical changes in the pyridinium moiety of the molecule and rupture of the nucleoside and nucleotide linkages. The loss of coenzyme function of DPN, the ability to function in hydrogen transport mechanisms by virtue of reversible hydrogenation of the quaternary nitrogen of the pyridinium base, is probably associated with the first of these reactions.

The labilization of the nucleoside linkage in ATP by the pyrophosphate group is shown by the identification of adenine as a product of the ultraviolet degradation of ATP, whereas adenosine and adenylic acid remained unchanged following exposure to ultraviolet radiation. The identification of adenine as a product of the decomposition of DPN indicates that the pyrophosphate linkage in this molecule exerts a similar effect.

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Hydrogen-bonding in Polyacrylate Solutions[1]

BY DAVID EDELSON[2] AND RAYMOND M. FUOSS

We recently[3] reported data on the conductance and viscosity of aqueous solutions of sodium polyacrylate and of poly-4-vinyl-*n*-N-butylpyridinium bromide. While conductances at the same equivalent concentration were not greatly different for these two polyelectrolytes, a striking contrast was observed in relative viscosity η_r. For example, at $c = 0.2873$ monomoles per liter, the relative viscosity for the polyacrylate was 230 while that for the polybromide at $c = 0.2737$ was only 8.0. Further experimental work has served to suggest an explanation of the difference.

The molecular weight of the polyacrylate was not known and cannot be determined by conventional methods. We therefore decided to prepare the methyl ester.

A 50-g. sample of the 16% aqueous polyacrylic acid was evaporated to dryness under low pressure; the residue was taken up in 50 ml. of methanol. After adding 1.5 ml. of sulfuric acid as catalyst, the solution was refluxed for eight hours; to hold the polymethyl acrylate in solution, 30 ml. of acetone were added during this time. After evaporation nearly to dryness at room temperature under vacuum, the residue was taken up in methyl ethyl ketone and the ester was precipitated as a gum by pouring the solution into water. After washing to remove sulfuric acid, the ester was dissolved in dioxane and recovered by sublimation of solvent from the frozen solution.[4] The product was slightly rubbery, but hardened after several days drying under vacuum at room temperature. A weighed sample was titrated in dioxane–water solution with standard caustic; residual acid was low, and indicated at least 85% esterification.

Viscosities of the ester were measured in dioxane solution. The results are given in Table I, where C is concentration in g./100 ml., and $\eta_{sp} = (\eta - \eta_0)/\eta_0$.

TABLE I

VISCOSITIES OF POLYMETHYLACRYLATE IN DIOXANE

C	η	η_{sp}/C
0.0000	0.01195	(2.35)
.1156	.01553	2.60
.2290	.01960	2.80
.470	.03022	3.26

The reduced viscosities are linear in concentration, with $k' = 0.336$, and extrapolate to an intrinsic viscosity of 2.35. Comparison with data for polymethylmethacrylate in benzene[5] and for polyvinylacetate in acetone[6] indicates a degree of polymerization of the order of 6000 for our polyacrylate. Since the polybromide had a degree of polymerization of 2000, and since reduced viscosity increases more slowly than molecular weight, the much higher viscosity of the polyacrylate can hardly be ascribed to its higher molecular weight alone.

Since, therefore, the high viscosity of the sodium polyacrylate solution presumably cannot be accounted for on the basis of long chains in the polyanion, some other explanation becomes necessary. Cross-linking of polyacrylate ions due to hydrogen bonds between carboxyl ions of different chains *via* water molecules would lead to a very high macroscopic viscosity. The critical test of

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[2] Post-doctoral Research Fellow, Yale University 1949–1950.

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this hypothesis would be to measure the viscosity of the polyacrylate in a solvent such as methanol, where cross bonds could not form: considered from the point of view of hydrogen bonding, methanol is monofunctional while water is bifunctional.

Sodium polyacrylate is insoluble in methanol. Tetrabutylammonium polyacrylate was therefore prepared by the following procedure:

A 50-g. sample of aqueous acrylic acid was evaporated to dryness as before, taken up in absolute methanol and standardized by titration with potassium hydroxide solution, using phenolphthalein as indicator; normality found, 0.391. Tetrabutylammonium hydroxide in methanol was prepared by shaking fresh silver oxide (washed with methanol) with a methanol solution of tetrabutylammonium bromide. After filtration, a sample of the solution was titrated with standard hydrochloric acid, using methyl orange; normality found, 0.0407. Equivalent volumes of the polyacrylic acid and of the tetrabutylammonium hydroxide solutions were then mixed and diluted to 0.01956 normal.

Viscosities of the quaternary polyacrylate in methanol were measured at several concentrations, with the results shown in Table II. (A lower range of concentrations than that of our previous work was used, in order to avoid possible complications due to mechanical entangling of the polyions.)

Table II

Viscosities of Tetrabutylammonium Polyacrylate in Methanol

C	η_r	η_{sp}/C	c	η_{sp}/c
0.6132	1.839	1.368	0.01956	42.9
.3054	1.532	1.742	.00974	54.6
.1479	1.302	2.042	.00472	64.0

A comparison of these results with the data of Table III for sodium polyacrylate in water over a comparable range of concentration shows that the aqueous solutions have a much higher viscosity. (Both weight and equivalent concentration scales are used because the monomer weights are so different: $CH_2CHCO_2N(C_4H_9)_4 = 313.5$ and $CH_2CHCO_2Na = 94.05$.) For example, at $C = 0.2$ g./100 ml., the aqueous solution has seven times the reduced viscosity of the methanol concentration; at $C = 0.01$ monomole per liter, the aqueous solution has 3.5 times the reduced viscosity of the methanol solution.

Table III

Viscosities of Sodium Polyacrylate in Water

C	η_r	η_{sp}/C	c	η_{sp}/c
0.2701	4.26	12.05	0.02873	113
.1397	3.26	16.18	.01486	152
.0708	2.56	22.0	.00753	207

Based on these experimental results, we therefore conclude that the unusually high viscosity of sodium polyacrylate solutions is due to cross-linking through hydrogen bonds with water molecules. This result is probably general; *i. e.*, polymers which contain groups which can bond to hydrogen will give much higher viscosities in water than in other protonic solvents because water is bifunctional.

As concentration is increased, the reduced viscosity concentration curve for the sodium polyacrylate in water goes through a minimum; our previous data give $\eta_{sp}/c = 450$ at $c = 0.0442$ and $\eta_{sp}/c = 800$ at $c = 0.287$. In this range of concentration, the volumes occupied by polyanions are beginning to overlap[3] and we would then expect hydrogen-bond cross-linking to have a tremendous effect on viscosity.

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Sulfonic Acid Esters of Sucrose

By R. C. Hockett[1] and Morris Zief

Although *p*-toluenesulfonyl (tosyl) and methanesulfonyl (mesyl) esters are important intermediates for the synthesis of iodo and anhydro sugars, it is surprising that sulfonic acid esters of sucrose have not hitherto been described in the literature. Raymond and Schroeder[2] report treating acetone solutions of trimesyl and tritosylsucrose with sodium iodide, but the starting materials were not isolated or described. In connection with a study of anhydride formation among sugars and polyhydric alcohols, the sucrose derivatives listed in Table I have been prepared by the present authors. Thus far it has not been possible to obtain these products in a crystalline condition. Even though these derivatives are amorphous, however, purification by several precipitations from acetone and water gave fairly pure compounds. These showed compositions, on analysis, that correspond very closely to those predicted for esters in which the degree of substitution is as indicated in the table.

Experimental

Octamesyl and Octatosylsucrose.—Mesyl or tosyl chloride (0.088 mole) was added in small portions to a stirred mixture of 3.42 g. (0.01 mole) of sucrose and 80 cc. of pyridine at 0°. The reaction mixture was stirred for three hours and was then allowed to stand at room temperature for twenty-four hours. The reaction product was poured with stirring into ice-water, the powdery product was filtered off, dried and dissolved in acetone. The acetone solution was decolorized, filtered, and poured with stirring into ice-water. After two more precipitations from acetone and water, colorless, amorphous powders were obtained.

Tritosylsucrose.—Tritosylsucrose, prepared from 0.01 mole of sucrose and exactly 0.03 mole of tosyl chloride under similar conditions, separated as a gum when the reaction mixture was poured into ice-water. A chloroform solution of this gum was washed with dilute sulfuric acid, saturated sodium bicarbonate solution and finally with

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[2] Raymond and Schroeder, U. S. Patent 2,365,776.