

Van Slyke amino-nitrogen (manometric) determinations gave values of maximal 0.07 per cent amino-nitrogen, indicating an average chain-length of at least a hundred units and a molecular weight average of at least 20,000.

The corresponding poly-aspartic acid was obtained by treatment of a solution of the poly-ester (VII) in glacial acetic acid with phosphonium iodide in a stream of hydrogen gas. It is slightly soluble in hot water, soluble in dilute alkali.

We found that careful treatment of the poly-aspartic acid ester with normal alkali does not affect the peptide linkages; it appeared, therefore, feasible to obtain the acidic poly- α -amino-acids by eliminating suitably chosen (β - or γ -) ester groups from the respective poly-esters through hydrolysis with dilute alkali instead of the hydrolysis of these (benzyl) ester groups by phosphonium iodide. Experiments on these lines were started some time ago but were interrupted by conditions here.

A polymeric substance, the properties of which suggest peptide structure, was obtained from the product of the reaction of thionyl chloride on N-carbobenzoxy-l-aspartic acid (II). On heating this reaction product to 165°, melting occurred with evolution of gas and formation of a glassy mass which gave a positive biuret reaction, a negative reaction for diketopiperazines, and yielded the theoretical amount of aspartic acid on hydrolysis.

On prolonged heating of l-aspartic acid at 200° according to Schiff⁵, a fraction not mentioned by him, insoluble in hot water, was obtained, giving a positive biuret reaction and having about 1 per cent of its total nitrogen in the form of amino-nitrogen. Hydrolysis of this product leads quantitatively to free aspartic acid. The structure of this polymer has not yet been clarified.

The experiments reported here are part of an investigation (cf. the thesis of one of us (A. B.) for the M.Sc. degree of this University) carried out in 1947. The conditions prevailing in Jerusalem during the present year [1948] have delayed the conclusion of this work.

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Aug. 20.

¹ Frankel and Katchalski, E., *Nature*, **144**, 330 (1939). Frankel Neufeld and Katchalski, E., *Nature*, **144**, 832 (1939). Frankel and Katchalski, E., *J. Amer. Chem. Soc.*, **64**, 2264, 2268 (1942).

² Frankel and Katchalski, E., scientific papers presented to Ch. Weizman on his 70th birthday, 24, 74 (Jerusalem, 1944). Katchalski, E., Grossfeld and Frankel, *J. Amer. Chem. Soc.*, **69**, 2564 (1947); **70**, 2094 (1948).

³ Bergmann and Zervas, *Ber.*, **65**, 1192 (1932).

⁴ Bergmann, Zervas and Salzmann, *Ber.*, **66**, 1288 (1933).

⁵ Schiff, *Ber.*, **30**, 2449 (1897).

Photosensitization by Vat Dyes

It is well known that cellulose fabrics dyed with certain vat dyes disintegrate on exposure to light¹. The experimental evidence suggests that a photosensitized oxidation of the cellulose is responsible. It is known that dyes do, in fact, photosensitize a number of reactions²; but no systematic survey of the field has been attempted, and the factors which determine the relative efficiencies of different dyes are not known. In a preliminary study of photosensitization, we have found that such dyes can initiate the

autoxidation of tetralin, and the polymerization of styrene.

A tungsten filament projection lamp (1 kW.) was used as light source in the polymerization experiments, and a hot mercury arc (350 W.) in the autoxidation. In the latter case the light was filtered through 1 cm. of a 10 per cent solution of ferric alum in 2N sulphuric acid to remove light of wave-length less than 3600 Å. The rates of reaction relative to pure tetralin and pure styrene are given in Table 1. The figures are approximate only, since many of the dyes fade, especially during the polymerization.

Table 1

Dye	Relative rate of oxidation $pO_2 = 650$ mm. $T = 25^\circ$	Relative rate of polymerization $T = 14^\circ$
Caledon Yellow 5G	25	26
Cibanone Yellow R	17.8	18.8
Cibanone Orange R	10.5	15.5
Cibanone Yellow 2GR	7.7	11.4
Caledon Golden Yellow GK	5.3	—
Cibanone Orange 6R	4.9	6.7
Caledon Red BN	2.4	9.5
Caledon Dark Blue G	1.2	20.0
Caledon Jade Green XN	1.0	5.5
Caledon Jade Green 2G	0.9	7.9
Caledon Orange 2RT	0.8	—
Caledon Gold Orange 3G	0.6	—
Caledon Dark Brown 2G	0.1	14.0

In Table 1 the dyes are arranged in order of activity for the autoxidation. This is closely similar to that for the 'tendering' activities of the dyes on cellulosic materials³. Both reactions probably have a common origin, namely, the formation of radicals by removal of hydrogen atoms from the substrate by the excited dye. The relative activities in the photopolymerization are not in the same order, and presumably a different mechanism is involved, for example, a direct transfer of energy.

In the case of the autoxidation the general mechanism seems to be established (see following communication), and it is possible to determine the quantum efficiency of the primary process. The following approximate values have been determined for $\lambda = 4500$ Å.

Table 2

Dye	Quantum efficiency for sensitization ($pO_2 = 100$ mm.)
Caledon Golden Yellow GK	0.0053
Anthanthrone	0.012
Caledon Red BN	0.0021

Comparison with Table 1 shows that for the most active dyes the quantum efficiencies must be very high—close to unity.

We anticipate that photosensitization by dyes may have wide applications, and we are at present engaged in their study.

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¹ For recent summary, see Turner, *J. Soc. Dyers and Col.*, **63**, 372 (1947).

² Rabinowitch, "Photosynthesis" (New York, 1945).

³ Boulton, private communication. Egerton, *J. Soc. Dyers and Col.*, **63**, 161 (1947). Haller and Wyszewianski, *Melliand Textilber.*, **17**, 217, 325 (1936).