

between this polymer and silanol groups may be of interest in explaining its chemotherapeutic action. In a preliminary communication², it has been shown that monosilicic acid in concentrations below 0.01 molar produces a bathochromic shift in the ultraviolet absorption spectrum of poly-2-vinylpyridine 1-oxide. A similar shift is not observed when monosilicic acid is added to 2-ethylpyridine 1-oxide. A slight shift in the spectrum of poly-4-vinylpyridine-1-oxide in the presence of monosilicic acid indicates that there is also some interaction between the 4-isomer and monosilicic acid. These deductions have been confirmed by viscosity measurements. The interaction presumably involves hydrogen-bond formation between the N-oxide group and the silanol group.

Nash, Allison and Harington³ have shown that there is also interaction between poly-2-vinylpyridine 1-oxide and polysilicic acid because a precipitate is formed when solutions of the two are mixed, and this again indicates hydrogen bonding. The implied correlation between hydrogen bonding and chemotherapeutic activity has been examined by synthesizing a number of other pyridine oxide polymers, and the ability of these and of poly-N-vinylpyrrolidone to precipitate polysilicic acid has been observed. The ability of each to counteract the cytotoxic effects of silica was measured by adding each polymer to a culture of peritoneal macrophages to which silica powder had been added and comparing the survival times of the cells. (These tests were carried out by Dr Beck and Miss Sack in the Institut für Lufthygiene, Düsseldorf.) The results are summarized in Table 1. There is apparently no correlation between the ability of a polymer to inhibit the cytotoxic effect of quartz and its ability to precipitate polysilicic acid.

Table 1

Polymer*	Precipitation with polysilicic acid†	Protective action against silica
Poly-2-vinylpyridine 1-oxide	+	Highly active
Poly-4-vinylpyridine 1-oxide	+	Some activity*
Poly-2-methyl-6-vinylpyridine 1-oxide	+	Inactive
Poly-3-ethyl-6-vinylpyridine 1-oxide	+	Highly active
Poly-3-methyl-2-vinylpyridine 1-oxide	-	Inactive
Poly-2- <i>n</i> -propenylpyridine 1-oxide	-	Inactive
Polyethylene-(2,6-pyridyl)-dicarboxylate 1-oxide (polyester)	-	Active
Poly-N-vinylpyrrolidone	+	Inactive

* 2 per cent w/v aqueous solutions.

† 0.02 molar aqueous solution.

Further studies (unpublished) on the effect of monosilicic acid on the viscosity of solutions of poly-2-vinylpyridine 1-oxide and poly-4-vinylpyridine 1-oxide indicate that, while the complex formed by the first polymer is stable up to 60° C, that formed by the second is much less stable above 20° C. It seems that loose interchain cross-links and links between proximate parts of a randomly coiled polymer chain are formed by monosilicic acid with poly-4-vinylpyridine oxide but that monosilicic acid is more intimately bound to poly-2-vinylpyridine oxide. Interaction between oxygen and alkyl group in 2-methylpyridine oxide has been demonstrated⁴. The type of bonding is probably present in poly-2-vinylpyridine 1-oxide because this polymer has a lower pK_a value than the 4-isomer. A model shows that the polymer structure would then be very compact with the oxygen atoms aligned so that monosilicic acid could become attached to the polymer by two or possibly three hydroxyl groups. Cross-linking would be less likely with poly-2-vinylpyridine oxide than with poly-4-vinylpyridine oxide.

It seems probable that the ability of poly-2-vinylpyridine oxide to exert a protective action against silica depends not merely on its ability to form a hydrogen bonded complex, for most N-oxides will form such com-

plexes, but on the stability of the complex which is formed.

This work was supported by the Asbestosis Research Council and the Science Research Council.

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Received September 13, 1967.

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Carcinogens in Chinese Incense Smoke

CONSIDERATION of the high incidence of naso-pharyngeal cancer among the Chinese¹ led us to search for carcinogenic constituents in condensates from burning Chinese incense. Using thin-layer and column chromatography, several polycyclic aromatic hydrocarbons, including 3,4-benzopyrene, have been detected by ultraviolet absorption spectra. The 3,4-benzopyrene content was estimated fluorimetrically² to be of the order 0.4 μg /stick of incense. The free radical content of the tar condensates was estimated by Dr A. Horsfield of Varian Associates Ltd. to be approximately 1.3×10^{15} stable electrons/g (comparable with the figure 1×10^{15} /g obtained for cigarette tar³).

A search for nitrosamines in the condensate by the polarographic method⁴ gave negative results, but the method of Preussmann *et al.*⁵, and the Griess reagent, gave a salmon pink spot, R_F 0.35, on thin-layer chromatography (hexane : ether : dichloromethane, 4 : 3 : 2).

The same colour was, however, obtained by spraying the plate with sulphanilic acid (1 per cent in 30 per cent acetic acid) without the need of previous irradiation and of the second component of the Griess reagent, 1-naphthylamine.

Nitrosamines do not give a colour with the sulphanilic acid reagent, but aromatic aldehydes give chiefly yellow colours. Furfuraldehyde which gives a slowly developing red colour similar to that of the unknown constituent of incense condensate has, however, a different R_F on thin-layer chromatography.

The colours given by aromatic aldehydes with sulphanilic acid should be borne in mind when applying the Griess reagent for the detection of nitrosamines according to the procedure of Preussmann *et al.*⁵.

We thank Professor K. Shanmugaratnam for the Chinese incense.

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