

Fig. 2 shows electron micrographs of the surfaces of two films from Fig. 1—those having the greatest and the least oxygen contents. It is evident that the film with the highest oxygen content has almost maintained the original grain size after ageing 20 months. Over the same period, the film with least oxygen content has experienced extensive grain growth.

We conclude that the rate of grain growth was markedly slowed down in these experiments and that the effect probably resulted from the presence of oxygen in the film.

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### Crystallization of Penicillin in the Solid Phase

DURING experiments on the hygroscopicity of penicillin salts, an unusual behaviour of substantially pure freeze-dried potassium benzylpenicillin was noted.

On exposure to air, the material absorbed moisture at a steady rate, up to a maximum content of 7–14 per cent, apparently remaining in the solid state. Then suddenly, the material shrank to a more compact form and began to lose weight. At first the loss was rapid and then it continued at a diminishing rate until the specimen returned to its original weight.

The time required for the uptake and subsequent loss of moisture was variable and depended on the temperature and relative humidity of the air, and on the weight and compactness of the specimen. A specimen weighing 0.1 g would usually take up moisture for about 4 h, and then completely lose it in about 18 h.

That the abrupt change which occurred at the point of maximum moisture content is a spontaneous crystallization of substantially amorphous material is evidenced by the changes in physical properties summarized in Table 1.

Table 1. CHANGES IN PHYSICAL PROPERTIES OF POTASSIUM BENZYL-PENICILLIN ON EXPOSURE TO MOIST AIR

Property	Freeze-dried specimen		Control specimen*
	Before exposure	After exposure	
Stability on heating at 120° C	Decomposed within 16 h	Stable for 96 h	Stable for 96 h
Heat of solution (cal/mole) (at concentration 0.055 M)	4,550 ± 130	910 ± 90	850 ± 90
Aggregate refractive index	1.56	1.58	1.58
Microscopic appearance between crossed Nicols	Almost entirely isotropic flakes	Largely crystallites evenly distributed in a mainly isotropic groundmass†	Well-formed crystals showing uniform extinction
X-ray diffraction pattern	Faint diffraction lines with broad halo of scattering at low angles of diffraction	More intense diffraction lines with much less intense halo	Very intense diffraction lines

\* Crystallized from aqueous butanol.

† Crystalline areas showing single crystal characteristics (that is, uniform extinction) also occurred in many flakes of exposed material, especially along the edges of the flakes.

A similar spontaneous crystallization was observed with freeze-dried specimens of sodium benzylpenicillin and potassium phenoxymethylpenicillin. No such phenomenon was observed when calcium or procaine benzylpenicillin, phenoxymethylpenicillin (free acid) or calcium phenoxymethylpenicillin was exposed to moist air.

We thank Dr. A. R. Alderman of the C.S.I.R.O. Division of Industrial Chemistry (now of the University of Adelaide) and Dr. M. E. Hargreaves of the C.S.I.R.O. Division of

Tribophysics (now of the C.S.I.R.O. Physical Metallurgy Section) for crystallographic examinations and for X-ray analyses, respectively. We also thank Dr. D. C. Grove of the United States Food and Drug Administration for unpublished crystallographic data on potassium benzylpenicillin.

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## CHEMISTRY

### Comparison of the Effect of Alpha- and Gamma-radiation on an Enzyme

EXTENSIVE investigations have been carried out on the effects of radiation on various organic polymers assuming that they could be regarded as model compounds for biological materials. Our previous work concerning the effects of gamma-rays on aqueous polymer solutions<sup>1-3</sup> revealed the existence of new effects resulting from the presence of water. Radiation-induced changes in the polymer may result either from the direct effect of the radiation on the solute molecules or from the indirect effect, that is, reactions of solute with reactive species such as hydrogen atoms, hydroxyl radicals or solvated electrons produced by irradiation of the water. The indirect effect becomes increasingly important as the concentration is reduced<sup>4</sup>.

The radiation-induced reactions in solutions of macromolecules can be considerably affected by the presence of relatively small amounts of certain chemical additives. Some of the possible protection mechanisms can be envisaged to include the following: (a) Energy transfer between an excited macromolecule and the additive, the molecule being chemically unaltered. (b) Electron transfer from the additive to the polymer to replace an ejected electron before chemical changes in the molecule can occur. (c) True repair of a polymer radical by hydrogen transfer from the additive. (d) Stabilization repair of a solute radical by reaction with additive or additive radicals, the additive becoming incorporated into the molecular structure; the radical in this case becomes stabilized by modification as distinct from true repair. (e) The additive may react with radicals produced in the solvent before these can attack and modify the polymer; in this case protection is offered against the indirect effect and radiation damage is reduced without involving the macromolecule.

Our early research was carried out with  $\gamma$ -radiation; the effects of the more densely ionizing  $\alpha$ -radiation on these systems is now being studied to provide a comparison between the effects of these two types of radiation and to point to possible differences in protection mechanisms. In the case of the densely ionizing  $\alpha$ -radiation, track effects (reactions of primary reactive species with each other in the  $\alpha$ -track before they have time to diffuse into the solution and react with the solute) have to be taken into account. This may lead to differences in the radiation effects on the macromolecules as well as on the protection.

The polymer solutions (polyvinylpyrrolidone, which is cross-linked in aqueous solution mainly by indirect action, and polyethyleneoxide, which is cross-linked mainly by the direct action of radiation) which we have investigated for  $\gamma$ -radiation do not lend themselves readily to a similar investigation using polonium-210  $\alpha$ -radiation. As an alternative system for this comparison, we have chosen solutions of yeast alcohol dehydrogenase. The irradiations were carried out with 0.1 ml. of 0.1 per cent solution in