CHEMISTRY LETTERS, pp. 137-140, 1973. Published by the Chemical Society of Japan

PHOTOLYSIS OF POLY-L-SILVER GLUTAMATE

Yosiaki KONISHI and Hiroshi SAIJO
Department of Chemical Engineering, Faculty of Engineering,
Tokushima University, Minami-Josanjima, Tokushima, Japan

The film of poly-L-silver glutamate was photolyzed when irradiated at wavelength 253.7 nm. With irradiation the surface of the film finally turned into a metallic mirror due to the photolytic silver. This result is interpreted by assuming the primary photochemical process associated with one electron transfer from the carboxylate ion to the adjacent silver ion.

It is well known that silver salts of various carboxylic acids photolyze and separate silver. Unlike the most silver salts of low molecular carboxylic acids, those of high molecular polycarboxylic acids can be prepared in films, which are more favorable for the study of the photolysis. We have previously investigated the photolysis of silver alginate in film state.[1-3] In that case the surface of the film turned into a metallic mirror due to the photolytic silver. The silver salt of poly-L-glutamic acid is also photolyzed by the ultraviolet irradiation and the surface turns into a metallic mirror, as in the silver alginate.

The film of poly-L-silver glutamate (PLSG) of about 3μ thickness was prepared in the following way. The aqueous solution of poly-L-sodium glutamate of 0.5 % was coated on glass or silica plates (1 ml/15 cm^2) and dried in the room air, then the plates were immersed in 0.1 N silver nitrate solution for an hour and washed with water to eliminate sodium nitrate and excess silver nitrate contained in the films, and dried again in the room air. PLSG is a colorless and brittle substance, and insoluble in water. The films were exposed at 3 cm distance from a sterilization lamp, which emitted the radiation of wavelength 253.7 nm strongly.

Absorption spectra of poly-L-glutamate are indicated in Fig.1. The silver salt has an absorption tail in the region of the wavelength of 240～300 nm, where

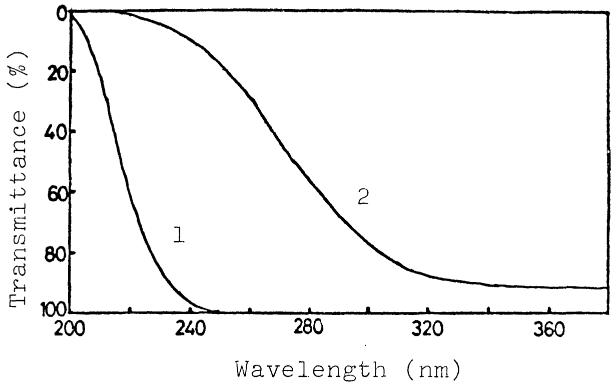


Fig.1. Absorption spectra of poly-L-glutamate. 1 : Na salt, 2 : Ag salt

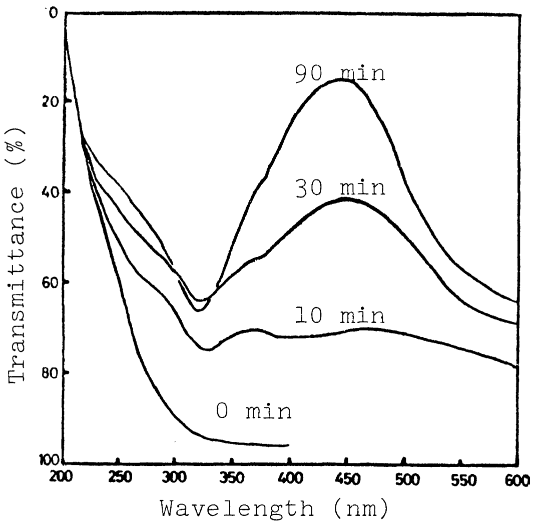


Fig.2. Changes of spectra of PLSG during UV irradiation.

the sodium salt has no absorption. Considering that both carboxylate and amide groups generally have no absorption above 240 nm in solution and that silver has a relatively high redox potential, the absorption in the range of 240～300 nm by the silver salt may be concerned with the direct transfer of one electron from the carboxylate ion to the adjacent silver ion. It seems, therefore, that the primary products of the photolysis of PLSG are a silver atom and an acyloxyl radical.

When the films of PLSG were irradiated with ultraviolet rays at room temperature, three new absorption bands were produced (Fig.2). These three bands appeared at 300, 360 and 450 nm respectively. In atomic spectrum of silver there exists the strongest absorption band at 328 nm. On the other hand, according to the radiolysis of a sulfuric acid glass containing silver sulfate at 77°K,4) It was found that a neutral silver atom, i.e., Ag^0 produced an absorption band at 313 nm. Furthermore, it was also found that a silver atom in the presence of a few near neighbours of silver ions, i.e., $Ag^0(Ag^+)_n$ absorbed near 350 nm in the same state. By comparing these results with ours, it seems that the two absorption bands at 300 and 360 nm may be attributed to a neutral silver atom Ag^0 and $Ag^0(Ag^+)_n$ (probably Ag_2^+ in our case) produced in the solid polymer, respectively. The existence of Ag^0 and Ag_2^+ in the irradiated polymer is in accord with expectation based on the assumed primary photochemical process of this polymer. The absorption band at 450 nm, which causes the film to be brown colored, can readily be considered as the result of plasma resonance of conduction electrons in colloidal silver particles.

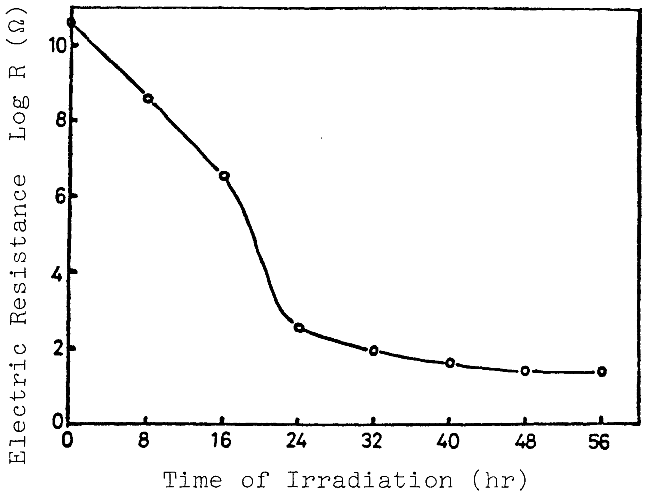


Fig.3. Curve of electric resistance vs. time of irradiation for PLSG film (ca. 3μ thick).

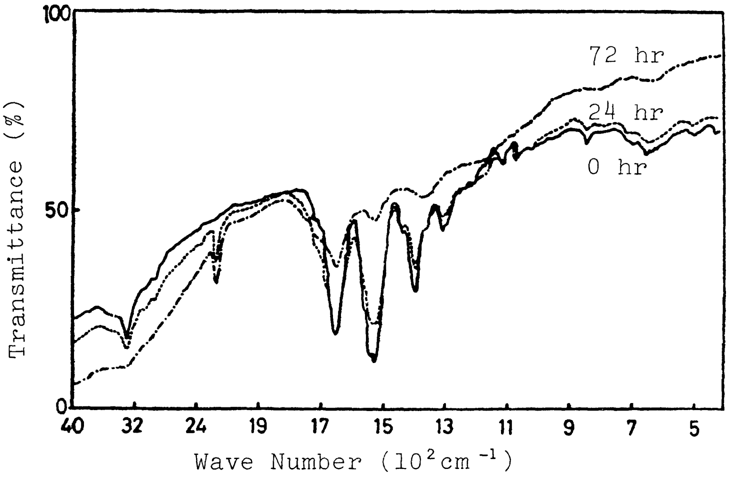
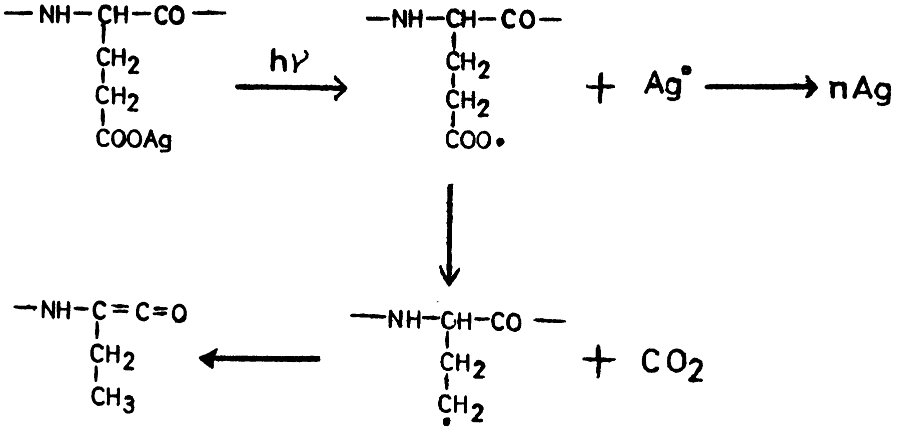


Fig.4. Changes of IR spectra of PLSG during UV irradiation.

The increase of this band with ultraviolet irradiation finally leads to the formation of a " metallic mirror " surface on the irradiated film. Accordingly, on prolonged irradiation, the electric resistance of the irradiated surface gradually decreases due to the photolytic silver from the original value, 10^{10} Ω/cm^2, to the final value, 10^1 Ω/cm^2 (Fig.3). Since there exists only a limiting amount of silver ions on the surface of the original film, it is suggested that photolytic silver atoms produced in the interior of the film migrate onto the irradiated surface and subsequently coalesce to form a very thin layer of metallic silver.

The infrared absorption spectra of PLSG before and after ultraviolet exposure are shown in Fig.4. It is found in this figure that the absorption at 1520 cm^{-1}, which can be attributed to the anti-symmetrical vibrations of the carboxylate groups, diminishes progressively with exposure time. This fact indicates that carboxylate groups and consequently ion pairs of carboxylate ions and silver ions in the silver salt disappear due to the primary photochemical process described above. On the other hand, it was confirmed by gas chromatography that PLSG evolved large amounts of carbon dioxide and traces of carbon monoxide, methane and ethane during ultraviolet exposure. Carbon dioxide seems to be formed by decarboxylation of the acyloxyl radical produced by the electron transfer process. It is also found in Fig.4 that a new absorption band appears at 2150 cm^{-1} during ultraviolet irradiation. In connection with its absorption region, it is reasonable to consider that a ketene is formed by a secondary reaction.

The summary of the results mentioned above may be shown schematically below.



REFERENCES

1) Y. Konishi, H. Hada, and M. Tamura, Nippon Kagaku Zasshi, 90, 992 (1969).

2) Y. Konishi, H. Hada, and M. Tamura, ibid., 92, 829 (1971).

3) Y. Konishi, H. Hada, and M. Tamura, ibid., 92, 1091 (1971).

4) D. M. Brown and F. S. Daiton, Trans. Faraday Soc., 62, 1139 (1966).

(Received December 4, 1972)