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ESR Study on Photodecomposition Mechanism of Oxidized Poly(vinyl Alcohol)

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Synopsis

Photolysis behavior of oxidized poly(vinyl alcohol) (PVA) in which carbonyl groups were introduced by oxidation with sodium hypochlorite and periodic acid was investigated by using ESR spectrometry. Increased formation of PVA radicals was observed in the sample with low degree of oxidation, which showed an emphasized formation of triplet component radical. On the other hand, the formation of radicals tended to be depressed in the highly oxidized sample, and a singlet component was dominant in the ESR spectrum. By examining infrared and ultraviolet spectra of the oxidized sample, the sample was found to contain two structures, a saturated ketone group and an α,β -unsaturated group; the latter structure was intensified with increasing degree of oxidation. Based on ESR studies of the photoirradiated acetone and mesityl oxide, the models of saturated and α,β -unsaturated ketone structures in the oxidized PVA, respectively, a photodecomposition mechanism of oxidized PVA was proposed.

INTRODUCTION

It is generally known that aliphatic carbonyl compounds are easily photolyzed by ultraviolet light. Some studies¹⁻³ on photolysis of polymeric materials activated by carbonyl groups present in the main chains have been reported. We analyzed ESR spectra of photoirradiated poly(vinyl alcohol) (PVA) to find the formation of three kinds of radical, showing singlet, quartet, and triplet spectra, depending on irradiation conditions.⁴ These were assigned to alkoxy and methyl radicals which originated from the acetyl group remaining in the sample, and to carbon radicals generated by abstraction of hydrogen from the α -carbon to the hydroxyl group, respectively.

Oxidation of PVA with various oxidizing agents,⁵⁻⁸ such as hydrogen peroxide, potassium permanganate, potassium dichromate, sodium hypochlorite (NaClO), and periodic acid (HIO₄), are known to lead to the introduction of carbonyl groups into the main chain. In the present paper, photoinduced radicals in NaClO- and HIO₄-oxidized PVA samples were investigated by using ESR spectrometry. The relationship between the oxidized states and the formation of radicals is discussed. Finally, photodecomposition mechanisms of the oxidized PVA are discussed on the basis of analysis of the ESR spectra of photoirradiated acetone and mesityl oxide as the models of the oxidized PVA.