[J. Phys. Chem., **98**, 11301-11307 (1994)]

[Lab. of Pharm. Physical Chemistry]

Spectrochemistry of Polycarbohydrate Free Radicals Generated by Argon Plasmolysis: Effect of Tertiary Structure on Free Radical Formation.

Masayuki Kuzuya*, Kazue Morisaki, Junji Niwa, Yukinori Yamauchi, Kaijun Xu

We report the first in-depth ESR study of plasma-induced polycarbohydrate radicals in powdered cellulose and amylose. The ESR spectra are largely different in pattern between the two anomeric polymers. The hydroxylalkyl radical at C₃ of the glucose units of amylose was not formed. However, the acylalkyl radicals were observed in both polycarbohydrates. This anomaly in amylose was rationalized in terms of spontaneous dehydration of the hydroxylalkyl radical formed at C₂ of the glucose units. It was also shown that the polycarbohydrate radicals were rapidly reacted with oxygen in air, unlike monocarbohydrate radicals. This difference could be ascribed to the difference in the polymorphic forms between polycarbohydrates and monocarbohydrates.

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[Lab. of Pharm. Physical Chemistry]

Mechanochemical Solid-State Polymerization. VII. The Nature of Hydrolysis of Novel Polymeric Prodrugs Prepared by Mechanochemical Copolymerization.

Shin-ichi Kondo, Katsuyuki Murase, Masayuki Kuzuya*

Hydrophilic polymeric prodrugs have been prepared by the mechanochemical copolymerization of methacryloyl derivatives of bioactive compounds with acrylamide. The alkaline hydrolysis of polymeric prodrugs has been examined. Though the degree of hydrolysis of polymeric prodrugs increases with increasing the content of hydrophilic monomer in the copolymer, there exists a limit to the degree of hydrolysis attainable. The rate of hydrolysis depended largely on the structural feature of the polymer hydrolyzate; the use of carbamoyl derivatives of bioactive compounds is valuable for improving the nature of hydrolysis.

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Plasma-Driven Molecular Weight Changes of Polymethylmethacrylate.

Junji Niwa, Masayuki Kuzuya•

We report the plasma-driven molecular weight changes of polymethylmethacrylate (PMMA) based on the systematic gel permeation chromatography (GPC) measurements. The GPC spectra of plasma-irradiated PMMA powder have shown the apparent decrease in the molecular weight as plasma-duration increases. However, one of the characteristics of plasma-irradiation is the fact that it is surface limited. Thus, the observed GPC spectra were deconvoluted into the two spectra for plasma-reactive surface layer and non-reactive bulk layer. It was found that the molecular weight of surface layer decreased very steeply, with an increase in the amount of reacted surface layers. Although the GPC spectral intensity of the reacted surface layer has shown a tendency to level off, its molecular weight continues to decrease as the plasma-duration increases.