Nature of Auto-oxidations on Plasma-induced Surface Radicals of Aromatic
Ring-containing Polymers as Studied by Electron Spin Resonance.
Masayuki KUZUYA,* Masami SUJITO and Shin-ichi KONDO

In this paper, we report the first ESR study on the peroxo radical formation of plasma-irradiated aromatic ring-containing polymers such as polycarbonate (PC), polyethyleneterephthalate (PET) and polimide (PI) by its exposure to air after Ar plasma-irradiation. The observed ESR spectral pattern in Ar plasma-irradiated PC and PET is characterized by a relative decrease in the lateral peaks on the outer side of both the higher and lower field of the major central peaks, which were derived from a cyclohexadienyl-type radical and a single broad line spectrum derived from dangling bond sites (DBS) at the surface cross-link region.

Mechanochemical Solid-state Polymerization. VIII. Novel Composite Polymeric
Prodrugs Prepared by Mechanochemical Polymerization in the Presence of
Pharmaceutical Aids.
Shin-ichi KONDO, Shouichi HOSAKA and Masayuki KUZUYA*

We carried out the mechanochemical polymerization of methacryloyl derivatives of acetoaminophen and 5-fluorouracil in the presence of lactose. This method quantitatively produces powdered polymeric prodrugs in which fine particles of lactose are homogeneously dispersed. It is difficult to prepare such a powdered polymeric prodrug by conventional solution polymerization. The rate of drug release of polymeric prodrugs increases with increasing content of lactose. These results suggest that lactose is homogeneously dispersed in the polymer. The present method seems applicable to a wide variety of pharmaceutical aids. If one takes the physicochemical property of pharmaceutical aids into consideration, novel polymeric prodrugs with a variety of drug release rates can be synthesized simultaneously with mixing.

Mechanochemical Solid-state polymerization. IX. Theoretical Analysis of Rate of
Drug Release from Powdered Polymeric Prodrugs in a Heterogeneous System.
Shin-ichi KONDO, Shouichi HOSAKA, Isao HATAKEYAMA and Masayuki KUZUYA*

We theoretically derived the rate equation of drug release from a simple model in a heterogeneous system. Two kinds of rate equations for drug release derived from two possible limiting cases, that the rate-determining step is a diffusion or hydrolysis controlled process, can predict the experimental results only up to 50% hydrolysis. The rate equation derived from a model considering both the diffusion and hydrolysis processes, however, can successfully predict the experimental results for several kinds of polymeric prodrugs. It is also shown that the diffusion coefficient and rate constant for hydrolysis calculated from this equation thoroughly express the character of the co-monomer. The rate equation derived from the model that considers both diffusion and hydrolysis is very useful to analyze drug release from various kinds of polymeric prodrugs in a heterogeneous system.

Hydrogen Bonds of Poly-[(n-alkyl methacrylate)-co-(methacrylic acid)]'s
in Dilute Solutions.
Akihiro NOGUCHI,* Yasushi MASUI, Kazunori ODA and Masayuki KUZUYA

The nature of the association of poly[(n-alkyl methacrylate)-co-(methacrylic acid)]'s (poly(RMA-co-MAA)'s) in dilute chloroform solutions was investigated by Fourier transform infrared (FT-IR) spectroscopy and the solution viscosity. The proportions (\(P_{\text{free}}\)) of free carboxyls increased with the length of the alkyl groups in RMA's and with the decreasing MAA composition. From the relationships between \(P_{\text{free}}\) and the effective concentration (\(C_{\text{eff}}\)) of carboxyls attached to the polymer chain, it was shown that the major substituent effects of the alkyl groups on the hydrogen bonds in the copolymers are the extension of the polymer chain and the steric effect on the association between carboxyls and ester groups. Also, from the features of the shrinkage of the polymer chains accompanied with the intrachain association of carboxyls it was suggested that the hydrogen bonds in the copolymers are formed chiefly between the neighboring sites along the chain.

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