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[Lab. of Pharm. Physical Chemistry]

**Plasma-induced Surface Radicals of Low Density Polyethylene (LDPE)
Studied by Electron Spin Resonance.**

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Plasma-induced low-density polyethylene (LDPE) radicals were studied in detail by electron spin resonance (ESR) by its comparison with ESR of high-density polyethylene (HDPE). The systematic computer simulation disclosed that such observed spectra consist of three kind of radicals, midchain alkyl radical (1), allylic radical (2) as discrete radical species, and a large amount of dangling bond sites (DBS) (3) at an intra- and intersegmental cross-linked region. One of the most special features unique to plasma-irradiated LDPE, however, is the fact that thermally stable DBS (3) is a major component radical instead of a midchain alkyl radical in HDPE. This can be ascribed to the difference in polymer morphology between LDPE and HDPE: branched structure with a large amount of amorphous region for LDPE and linear structure with a large amount of crystalline region for HDPE. Thus, the nature of radical formation of PE was found to be affected by the polymer morphology in a very sensitive manner.

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**Peroxy Radical Formation from Plasma-induced Surface Radicals of
Polyethylene as Studied by Electron Spin Resonance.**

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The nature of peroxy radical formation from plasma-induced surface radicals of polyethylene (PE), both low-density polyethylene (LDPE) and high-density polyethylene (HDPE), was studied by electron spin resonance with the aid of systematic computer simulations. It was found that peroxy radical formation varies with the structure of component radicals of plasma-irradiated PE, both LDPE and HDPE. Among three plasma-induced radicals of PE, dangling bond sites (DBS) undergo an instant conversion into the corresponding peroxy radicals in contact with oxygen, while the midchain alkyl radical is of very low reactivity with oxygen in both LDPE and HDPE. Computer simulations disclosed that ESR spectra of peroxy radicals are similar to each other in LDPE and HDPE, both being composed of two types of spectra, a partial *g*-averaging anisotropic spectrum and a nearly isotropic single line spectrum due to different molecular motional freedom at the trapping sites of peroxy radicals.

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**Non-aqueous Capillary Zone Electrophoresis Using Polyethylene Glycol as a
Matrix Agent.**

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Non-aqueous capillary zone electrophoresis in acetonitrile containing polyethylene glycol as a matrix agent was investigated. Separation of benzoate anions as model samples were optimized by a control of the concentration and the selection of the chain length of polyethylene glycol. Base line resolution was attained in the presence of 15 % (w/v) polyethylene glycol 4000 for the benzoates used. In acetonitrile, polyethylene glycol works as a hydrogen-bonding donor and acceptor; the terminal hydroxyl groups serve as a donor toward the dissociated carboxyl groups of the benzoates, while the ether oxygen atoms serve as an acceptor toward the hydrogen-donating substituents of the benzoates. This property of polyethylene glycol is marked contrast with that observed in aqueous phase, where polyethylene glycol works predominantly as just a hydrogen acceptor. Quantitative analysis of the interaction is presented.

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[Lab. of Pharm. Anal. Chem.]

Hydrogen-bonding Interaction-assisted Capillary Electrophoresis.

Yukihiro ESAKA*

Capillary electrophoresis using polyethers as hydrogen-accepting agents was developed. The addition of PEG as a matrix agent in CZE causes a selective decrease in the electrophoretic mobility of some substituted benzoates having hydrogen-donating substituents. The addition of non-ionic surfactants with polyether structure to an SDS system for MEKC results in a selective increase in the relative capacity factors of some non-ionic and cationic-substituted benzenes with hydrogen-donating substituents. These effects can be interpreted in terms of a hydrogen-bonding interaction between the ether oxygen atoms of the polyether agents and the substituents of analytes. Separation was well controlled by adjusting the PEG concentration and mixing ratio of the surfactants. The thermodynamic aspects of these separation systems are discussed in detail.