〔J. Polym. Sci., Part A : Polym. Chem., **30**, 379-387 (1992)〕 [Lab. of Pharm. Physical Chemistry]

Nature of Plasma-Induced Radicals on Crosslinked Methacrylic Polymers Studied by Electron Spin Resonance.

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Plasma-induced radicals of several crosslinked methacrylic polymers such as poly (ethyleneglycol dimethacrylate) (PEDMA), poly (2-hydroxyethylmethacrylate) (PHEMA) and polymethacrylamide (PMAAm) were studied by ESR. All the spectral feature can be represented by "nine-line spectra" as a major spectral component similar to those of linear methacrylic polymers such as polymethacrylic acid (PMAA). A pronounced effect of crosslinking has emerged on the specific formation in the radical structure and the stability of radicals formed, especially in PEDMA. The formation of fewer kinds of radical in PEDMA is apparently caused by the high degree of crosslinking which leads to suppression of the occurrence of depolymerization on plasma irradiation.

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Nature of Mechanoradical Formation and Reactivity with Oxygen in Methacrylic Vinyl Polymers.

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The formation of mechanoradicals under anaerobic condition and their reactivity with oxygen at room temperature is described for several methacrylic polymers. The ESR kinetics of the mechanoradical formation of polymethylmethacrylate (PMMA) and polymethacrylamide (PMAAm) exhibit an interesting contrast. The discrepancy has been ascribed to mechanoradicals of PMAAm that are strongly stabilized by intermolecular and intramolecular doubly hydrogen-bonded networks among the amide groups. The mechanoradicals of both PMAAm and PMAA do not give a single peroxy radical, but rather a mixture of the mechanoradical and peroxy radical even after exposure to air, while the mechanoradiacals of other polymers are rapidly converted to the corresponding peroxy radicals.

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ESR Study on the Nature of Oxygen Plasma-Induced Surface Radicals of Teflon and Corresponding Peroxy Radical Reactivity.

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Oxygen plasma irradiation on powdered Teflon produces four kinds of radicals : midchain radicals, endchain radicals, immobilized dangling-bond sites (DBS) and their corresponding peroxy radicals. The effect of oxygen plasma irradiation on the radical formation was much lower than that of argon plasma irradiation. The ratio of DBS formation to total radical formation by oxygen plasma irradiation was to such a compatible extent as that by argon plasma irradiation. The increase in the rate of degradation induced by plasma irradiation was much lower than those of other hydrocarbon polymers. This specificity has been ascribed to a lower efficiency for the unsaturated-bond formation in the polymer main chain due to a large dissociation energy of a C-F bond.