〔J. Polym. Sci., Polym. Lett. Ed., **23**, 69 (1985)〕

Mechanism of Plasma-Initiated Polymerization: Experimental Evidence for the Postpolymerization Induced by Plasma-Generated Radicals Trapped on Glass Surface.

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In our previous publications, we have shown that the plasma effluent gas, which contains an allylic radical, induced very effectively the plasma-initiated polymerization of methacrylate and acrylate vinyl monomers. However, the question as to why the postpolymerization proceeds only with initially generated radicals remains unanswered. We report here experimental evidence that the plasma-generated radicals on a glass surface, which are extremely long-lived, are responsible for the lifelike postpolymerization in the plasma-initiated polymerization of methyl methacrylate.

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Reactivities of Carboxylic Acid Vinyl Monomers Differentiated by the Aggregation Forms and their Simple Molecular Orbital Interpretation.

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Plasma-exposed solution polymerizations of carboxylic acid vinyl monomers 〔methacrylic acid(MAA) and acrylic acid (AA)〕 in carbonyl solvents were found to be highly efficient, particularly in high-temperature postpolymerizations. Obviously the carbonyl solvents and/or the increased temperature caused the monomer aggregates to accelerate the rate of polymerization.

The molecular orbital features of the simple models of monomer aggregates of MAA and AA, supported by the CNDO/2 method, were capable of distinguishing the variations in the reactivities of the aggregates; the open-dimer was shown to be responsible for the enhanced reactivities under the abovementioned conditions.

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Plasma-generated Radicals Trapped on Glass Surface and their Reactivities.

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An inorganic plasma exposure with short duration of the various glass substrate such as hard (Pyrex), neutral and soft glasses, generated stable paramagnetic centers, and were all detected by ESR spectra. The electronic structure of the center was presumed to be a "hole trap" of the glass substrate. On the other hand, an organic plasma exposure of the same glasses under the similar conditions as above produced an ultrathin polymer film on the glass surface in the glow region, in addition to the above mentioned paramagnetic centers. It was shown that the glass surface thus treated can be functionalized with high catalytic activities for radical reactions and used for an initiation of the radical polymerizations.