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Mechanistic Insight into Immobilization and Release of Active Radical Species on a Novel Plasma-Driven Ultrathin Film

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Mechanism for immobilizing an active radical species and its slow release on a novel plasma-driven ultrathin film was proposed with the aid of molecular orbital calculations, which involves the existence of non-optimized weakened σ-bonds in such a ultrathin film and the propensity of their facile bond-cleavages.

We have recently reported that a novel plasma-driven ultrathin film prepared from a brief plasmolysis of several hydrocarbons (e.g., n-hexane, cyclohexane, propenetetramer, 1,5-hexadiene and various benzene-based compounds) and/or oxygen-containing organic vapors (e.g., allyl alcohol, methylisobutyrate, acrylic and methacrylic derivatives) in a closed system, which all favor to generate the plasma-fragmented species possessing unsaturated bond units, exhibited the high radical reactivities for initiating the radical chain polymerization of various conventional vinyl monomers such as acrylic and methacrylic acid including their ester, amide and nitrile derivatives, if one selects the proper solvent (either an organic solvent in solution polymerization or a vinyl monomer itself in bulk polymerization) as an initiation activator (Fig. 1),[1-6] while the ultrathin film similarly prepared from a plasmolysis of several nitrogen-rich organic vapors such as dimethylhydrazine, several alkyl amines and nitrile derivatives did not show such a radical reactivity.

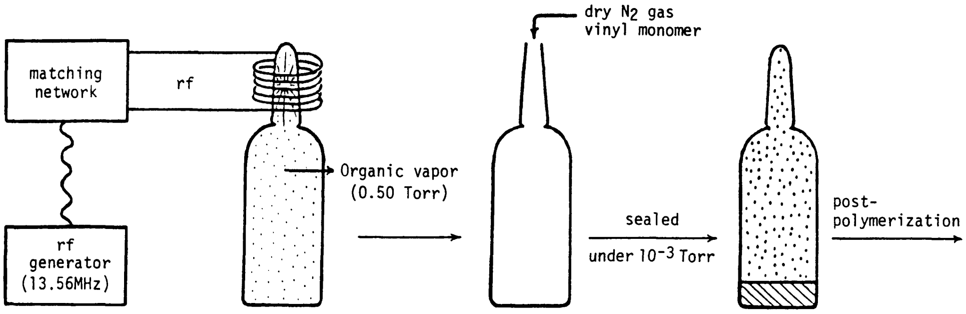
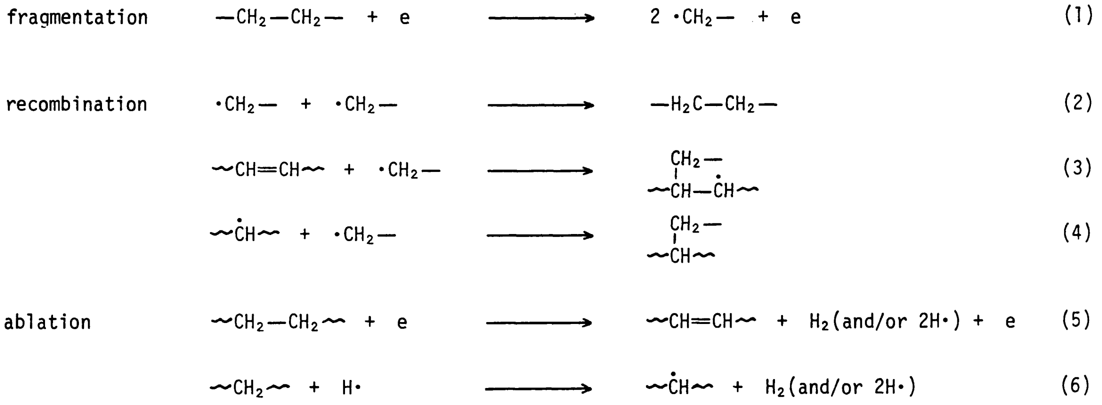


Fig. 1. Schematic representation for the polymerization in a plasma-exposed glass ampule.

It was also shown that such a film underwent the facile spin adduct formation of carbon-centered radicals for a long period of time in reaction with a spin trap such as phenyl t-butylnitrone in benzene, although these ultrathin films are diamagnetic based on the ESR spectral measurement.[2,7] This is a sharp constrast to a conventional plasma-polymerized film formed in the plasma-state polymerization which contains a large amount of free radicals (dangling-bond sites),8) although these radical centers are lack of the chemical reactivities. Based on these facts, it appears that active radical species has been slowly leached out of such a diamagnetic ultrathin film.

We wish to report here one rationalization to interpret the above-mentioned physicochemical properties unique to the plasma-driven ultrathin film with the aid of the molecular orbital calculations of some model compounds as well as taking a characteristics of a plasma process for the film deposition into account.

A variety of organic plasma-exposed glass ampules where the plasma-driven ultrathin film was deposited were capable of inducing the spin adduct formation as well as the polymerization of various vinyl monomers even several weeks after plasma exposure. Thus, it can be considered that the some special structural features of such an embryonic type of the organic plasma-driven ultrathin film is responsible for immobilizing active radical species so as to stabilyze it and quench the paramagnetic center. This must be associated with an unique plasma process for the film deposition on the solid surface directly from the gas phase through an atomic process of a variety of the plasma-fragmented species including the concurrent ablation process so that the resulting plasma-driven film is completely amorphous and is not composed of the repeating units of the monomers. A series of these representative reactions for a plasma-polymerization were schematically summarized in Fig. 2.



fragmentation

$$-CH_2-CH_2- + e \longrightarrow 2\,\cdot CH_2- + e \quad (1)$$

recombination

$$\cdot CH_2- + \cdot CH_2- \longrightarrow -H_2C-CH_2- \quad (2)$$

$$\sim CH{=}CH\sim + \cdot CH_2- \longrightarrow \sim\underset{}{\overset{CH_2-}{CH}}-\dot{C}H\sim \quad (3)$$

$$\sim\dot{C}H\sim + \cdot CH_2- \longrightarrow \sim\overset{CH_2-}{CH}\sim \quad (4)$$

ablation

$$\sim CH_2-CH_2\sim + e \longrightarrow \sim CH{=}CH\sim + H_2(\text{and/or } 2H\cdot) + e \quad (5)$$

$$\sim CH_2\sim + H\cdot \longrightarrow \sim\dot{C}H\sim + H_2(\text{and/or } 2H\cdot) \quad (6)$$

Fig. 2. Representative reaction scheme for plasma-polymerization.

We suggest here that there exist some of reaction centers which are not optimized from the sp^2 carbon to the sp^3 carbon during the film formation by recombination of the plasma-generated radicals with some of the double bonds (Eq. 3 in Fig. 2) and/or the dangling-bond sites (Eq. 4 in Fig. 2) presented in the film surface, due to the restriction of the spacial flexibility of the centers in the amorphous framework and network structure of the film. Consequently, an embryonic stage of the plasma-polymerized film is forced to contain nonoptimal geometrical units consisted of C_{sp2}-C_{sp3} and/or C_{sp2}-C_{sp2} σ-type bonds due to retaining the geometrical features prior to the bond formation.

In order to evaluate this type of destabilization caused by the nonoptimization from $C_{sp}2$ to $C_{sp}3$ on the bond formation, we have carried out semiempirical molecular orbital calculations supported by the UMINDO/3 method[9] for the assumed-ethane formation from two methyl radicals as the simplest radical recombination model system.

The results were shown in Fig. 3 and indicated that the single inhibition to sp^3 carbon of the carbon-carbon bond has destabilized the nonoptimal ethane by as much as ca. 1.4 x 10^2 kJ/mol relative to an ethane of the full optimized geometry retaining normal $C_{sp}3$-$C_{sp}3$, and that the C-C atomic bond population at each of the optimal C-C bond distance also diminished according to such a structural features as shown in the parentheses of Fig. 3, resulting in the formation of weakened σ-bond.

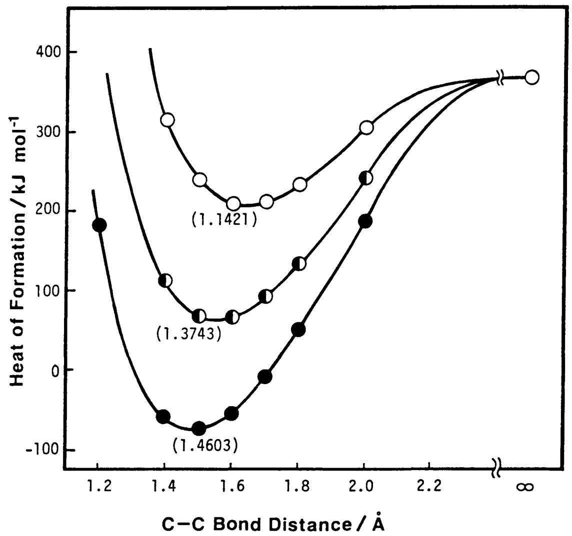


Fig. 3. Effect of orbital-hybridization on the ethane formation from two methyl radicals at various C-C bond distances calculated by the UMINDO/3 method. —○—; $C_{sp}2$-$C_{sp}2$, —◐—; $C_{sp}3$-$C_{sp}2$, —●—; $C_{sp}3$-$C_{sp}3$. The number in parenthesis is Atomic Bond Population at each of optimal C-C bond distance.

It is also widely accepted that the concurrent ablation process such as hydrogen elimination at the surface of the deposited film to creat the unsaturated bonds (Eq. 5 in Fig. 2) and/or dangling bond sites (Eq. 6 in Fig. 2) is of general occurrence during the film formation in the plasma process, since the ratio of hydrogen to carbon in the resulting polymeric film is always observed to be lower than in the starting organic compounds for plasmolysis. It can be considered here that the carbons of unsaturated bonds produced in this process are not always optimized to sp^2 carbon due to the geometrical restriction of the sp3 carbon presented in the film framework. In fact, the molecular orbital calculation for non-optimized $C_{sp}3$-$C_{sp}3$ ethylenes as a model compound indicated the destablization as much as 1.6 x 10^2 kJ/mol relative to the optimized ethylene.

Thus, the ablation process also produced the unsaturated bonds units weakly bonded with the polymer film framework. This is also consistent with the fact that the ultrathin film prepared from a plasmolysis of olefinic vapors exhibited the higher radical reactivity. Furthermore, we have recently obtained some supportive evidence on this point that the radical reactivity was in fact enhanced by a brief helium plasma exposure on the ultrathin film. This can be attributed to creating distorted double bond by the ablation process such as molecular hydrogen elimination, since non-reactive plasma such as helium is known to be especially effective for ablation of various solid surface.

On the other hand, it is known that pyramidal-pyramidal nitrogen inversion is very rapid since its energy barrier is very small due to lower electronic repulsion among the substituents bonded with nitrogen atom. In fact, the molecular orbital calculation for this process indicated that the energy difference between the planar ammonia and optimized pyramidal ammonia is only ca. 21 kJ/mol. In this sense, weakened carbon-nitrogen bonds are not introduced to the nitrogen-containing plasma-driven ultrathin film, even if the distorted amino moieties were presented in such a film.

We believe that the presence of these types of weakened carbon-carbon bonds in the ultrathin film and the propensity of their facile bond-fissions is responsible for the observed radical reactivity that active radicals are slowly leached out of the film matrix as a variety of species in structural and molecular-weight terms as the film is gradually dissolved and/or swollen in a solvent. And, the nitrogen-containing ultrathin film prepared from a plasmolysis of nitrogen-rich organic compounds does not contain the weakened carbon-nitrogen bond, accounting for the difference in radical reactivity between nitrogen-containing and non-nitrogen containing plasma-driven ultrathin film (vide supra).

Thus, the mechanism reported herein seems to be consistent with all experimental facts thus far obtained relevant to the plasma-driven ultrathin film.

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