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ESR Spin-Trapping Technique for Partial Structural Characterization of the Radicals Leached Out of a Plasma-Driven Ultrathin Film

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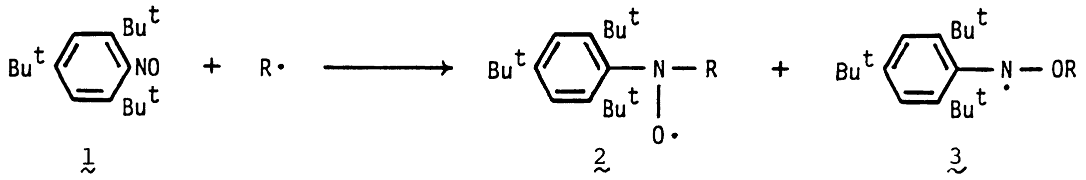
The partial structure of the radicals leached out of a plasma-driven ultrathin film was characterized by the ESR spectral measurements with the aid of computer simulations obtained from the reactions for 2,4,6-tri-t-butylnitrosobenzene (BNB) spin-adduct formation in various organic plasma-exposed glass ampules.

In connection with the fact that certain organic plasma-exposed glass surfaces where an ultrathin film was deposited can effectively induce the polymerization of various vinyl monomers,[1-5)] we have recently reported the nature of radical reactivity of such glass surfaces studied by the ESR spin-trapping techniques using a solution of phenyl-t-butylnitrone (PBN) as a spin trap.[3,6)] It was found that the PBN spin adducts trapped by carbon-centered radicals were obtained in such reactions. Spin-adduct formation continued to occur over a long period of time, demonstrating that such a glass surface can undergo a constant slow release of radical species. A kinetic study indicated that the rate-determining step for the formation of the spin adduct is the stage when an active radical species is leached out of the ultrathin film. Thus, the mechanism by which the ultrathin film immobilizes the active radical species and permits its slow release was ascribed to the presence of weakened σ-bonds in the unique ultrathin film and their facile bond fission by physicomechanical action of the solvents used.[4,7)] However, we were not able to obtain any information concerning the structure of trapped-radicals from the ESR spectra because of small difference in the hyperfine splitting constants among the adducts obtained although a variety of active radicals in either structural or molecular weight terms may be leached out of the ultrathin film formed in the plasma polymerization.

Nitrso-compounds are also widely used as another kind of spin trap, which has two trapping sites, the nitrogen and oxygen atoms of the nitroso-group, depending on steric interference around the radical center in the trapped-radical, and shows the hyperfine splitting by the hydrogen atom attached to the trapped-radical center adjacent to the nitrogen or oxygen atom of the spin adduct. It is, therefore, possible to determine the partial structure of the trapped radicals. It is known that 2,4,6-tri-t-butylnitrosobenzene (BNB) (**1**) can react with primary alkyl radicals to form exclusively nitroxides (**2**), and N-alkoxy-anilino-radicals (**3**) are not detected at all. Most of secondary alkyl radicals add at the nitrogen atom of BNB to give nitroxides (**2**), although some radicals can add to the oxygen atom to give anilino-radicals (3). Tertiary alkyl radicals attack the nitroso-group at the oxygen atom exclusively to afford anilino-radicals (3).[8] Thus, BNB spin-trapping technique should be useful in elucidating the structure of the radicals leached out of a plasma-driven ultrathin film.



We have carried out a number of reactions for BNB spin-adduct formation in plasma-exposed glass ampules prepared from a brief plasmolysis of various organic vapors which had afforded the PBN spin adduct, and the ESR spectra were recorded by JES-FE1XG (JEOL) according to the procedure shown in Fig. 1.

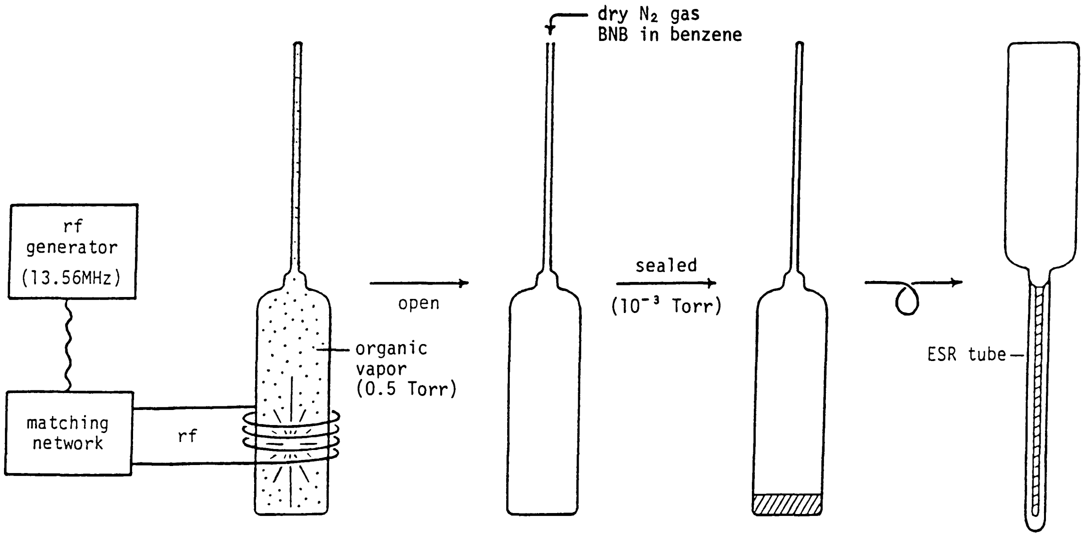


Fig. 1. Schematic representation for ESR spectral measurements of the BNB spin adduct. The plasma state was sustained for 60 s by radio-frequency (rf) discharges of inductive coupling with 50 W operating at 13.56 MHz.

We report here the partial structural characterization of such radicals by means of the analyses of the ESR spectra with the aid of computer simulations.[9] In fact, the BNB spin adduct was observed by the ESR spectral measurement and the spin-adduct formation continued to occur over a long period of time in all the cases examined.

Figure 2 shows several selected ESR spectra of the BNB spin adducts in steady state obtained from BNB benzene solution in plasma-exposed glass ampules prepared from a brief plasmolysis of toluene (A), methyl methacrylate (B) and styrene (C) together with the corresponding computer-simulated spectra (D),(E) and (F). It is clear from Fig. 2 that spectra (A) and (B) are similar to each other. It was found with the aid of computer simulation that these two spectra consisted mainly of anilino-radicals (3) trapped by tertiary alkyl radicals, and mixed with small amount of nitroxides (2) trapped by primary and secondary alkyl radicals (ca. 1:1:7 for (A) and ca. 1:2:8 for (B) in the ratio of spin number from primary to tertiary). The spectra similar to those were also obtained from the reactions in plasma-exposed glass ampules prepared from many other hydrocarbons such as n-hexane, 4-methyl-1-pentene, 1,5-hexadiene and ethylbenzene.

On the other hand, it can be seen that the spectrum (C) is far more complicated, and largely different from the spectra (A) and (B). Likewise, the effort for the computer simulation disclosed that the observed spectrum is composed of the BNB spin adducts of nitroxides (2) trapped by primary and secondary alkyl radicals, and anilino-radicals (3) trapped by tertiary ones with ca. 1:7:7 in the ratio of spin number.

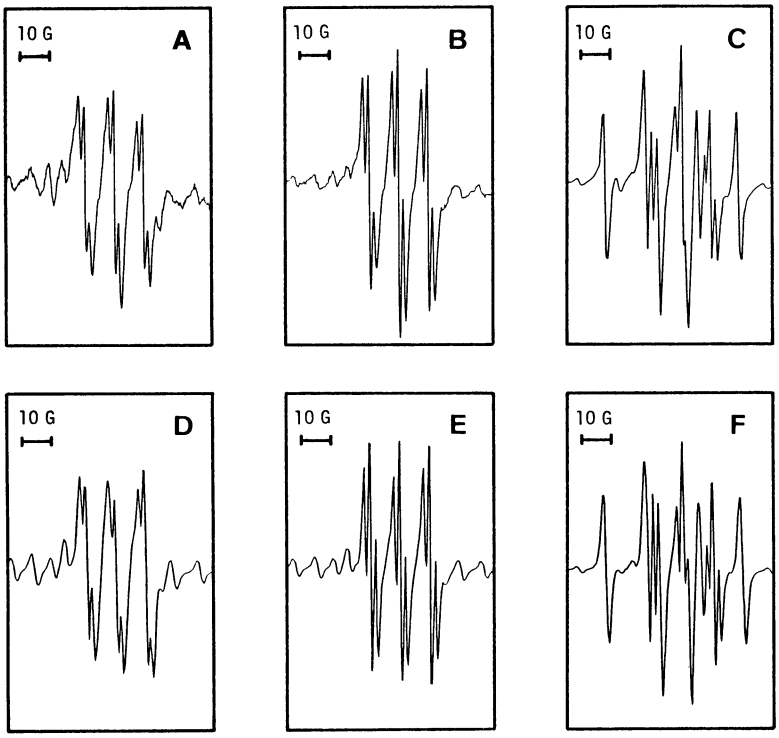


Fig. 2. ESR spectra of the BNB spin adduct obtained from toluene-(A), methyl methacrylate-(B) and styrene-derived ultrathin film (C), together with the corresponding simulated spectra (D), (E), and (F).

These results clearly indicated that a variety of radical species were leached out of the film, and the structure of the compounds for plasmolysis reflected, at least, partially on the structure of the ultrathin film obtained at a very initial stage of plasma polymerization, although plasma-polymerized film is generally considered structureless. When considering that a styrene molecule possesses secondary, tertiary and quaternary carbon atoms in the ratio of 1:6:1, which can be considered to convert correspondingly into the primary, secondary and tertiary radicals in plasma reaction, the above results also indicated that the elimination of hydrogen atoms from the compounds used for plasmolysis occurred considerably.

Furthermore, the spectra (G)-(I) recorded at earlier stage of the reaction giving the steady-state spectra (A)-(C) were shown in Fig. 3. Comparison of these spectra (G)-(I) with the spectra (A)-(C) clearly shows that the spectral features are apparently different from each other, respectively, and the ratio of the spin adducts trapped by tertiary alkyl radicals grows up as the reaction

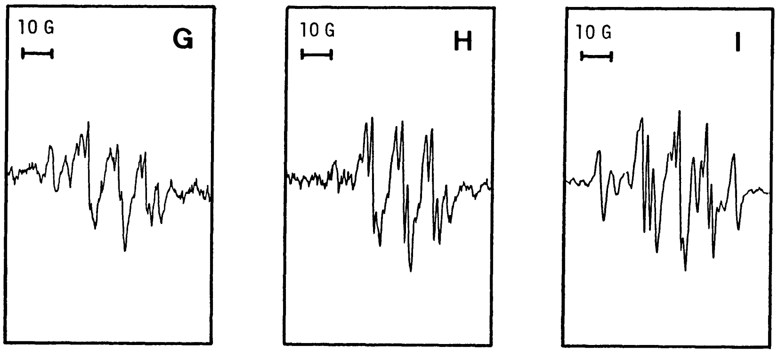


Fig. 3. ESR spectra of the BNB spin adduct obtained from toluene-(G), methyl methacrylate-(H) and styrene-derived ultrathin film (I) recorded at the earlier stage of each reaction.

proceeds, demonstrating that tertiary radicals are rather late in leaching out of the film.

All these results are entirely consistent with structural features of plasma-polymerized film derived from general occurrence in the plasma polymerization, and we believe this is the first presentation concerning the structural elucidation of the radicals leached out of plasma-polymerized films.

References

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9) The computer simulations were performed using a micro computer (NEC PC-9801 Vm2) according to the following procedure; First, we obtained three typical simulated ESR spectra of BNB spin adducts trapped by primary, secondary and tertiary alkyl radicals using Lorentzian line under the consideration of the reported data of the g-value, hyperfine splitting constant and half height width for each spin adduct.[8] A number of critical points of the observed spectrum to represent the spectral feature were digitized using MITABLET-II (Graphtec Co. Ltd.). Then, based on these data, the simulated spectrum was obtained by fitting iteratively for the data of X-axis (magnetic field) followed by those of Y-axis (spectral intensity) according to non-linear least sqaure method to determine the ratio of spin number (molar ratio) of each spectrum.

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