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Structural Features of the Radicals Leached out of a Plasma-Driven Ultrathin Film in Molecular Weight Terms

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Structural features of the radicals leached out of a plasma-driven ultrathin film in molecular weight terms were presented based on the permeability of such radicals to initiate the aqueous solution-polymerization of acrylic acid on the specially designed experiment.

It seems well established that the physicochemical properties of the novel invisible ultrathin film which is formed at a very initial stage of plasma polymerization is decidedly different from those of well-known plasma polymerized films, "soft film" and "hard film",1) and can be considered as the third type of plasma-polymerized film, which we refered to as "embryonic film".2) This type of ultrathin film, unlike normal plasma-polymerized film, is diamagnetic based on the ESR spectral measurement,3) but is of high radical reactivity on contact with appropriate solvents.3-6) Thus, it was demonstrated that the ultrathin film deposited on a plasma-exposed glass surface prepared from several hydrocarbons and/or oxygen-containing organic compounds under a brief plasma exposure not only exhibited a catalytic effect for initiating the radical chain polymerization of various conventional vinyl monomers,4-6) but also afforded a large amount of the spin adduct of phenyl-t-butylnitrone (PBN) on its treatment with the benzene solution over a long period of time.3,7)

In this connection, we have reported the partial structural characterization of the radicals leached out of such a film by the ESR spin-trapping techniques using a solution of 2,4,6-tri-t-butylnitrosobenzene (BNB) as a spin trap. It was found with the aid of computer simulation that the ESR spectra consisted mainly of the spin adducts trapped by tertiary alkyl radicals and mixed with a small amount of other alkyl radicals such as primary and secondary radicals in all the cases examined, regardless of the nature of organic vapors for plasmolysis, and that a variety of radical species were in fact leached out of such films.8)

We have explored the molecular weight (or molecular size) of the radicals leached out of the film as another interesting structural features, and wish to present here the experimental evidence that such radicals are of high molecular weight, i.e. macroradicals, and are distributed over a wide range of molecular weight based on the results of the specially designed polymerization of acrylic acid (AA).

Figure 1 illustrates the model scheme for the method of polymerization examined. Fundamental device of this experiment is that aqueous solution containing the monomer of AA was divided to two layers by dialysis membrane. And, if the active radicals are of low molecular weight enough to permeate through the membrane, the radical concentration should be identical between the two layers. Then, the polymerization of vinyl monomers would equally proceed in both layers, and being such the case of polymerization of AA by use of conventional radical initiator such as azobisisobutyronitrile (AIBN). However, if the active radicals initially presented in only one layer are of large molecular weight, they can not permeate through the membrane, resulting in different concentration of available radicals. Thus, the rate of polymerization would differ between the two layers.

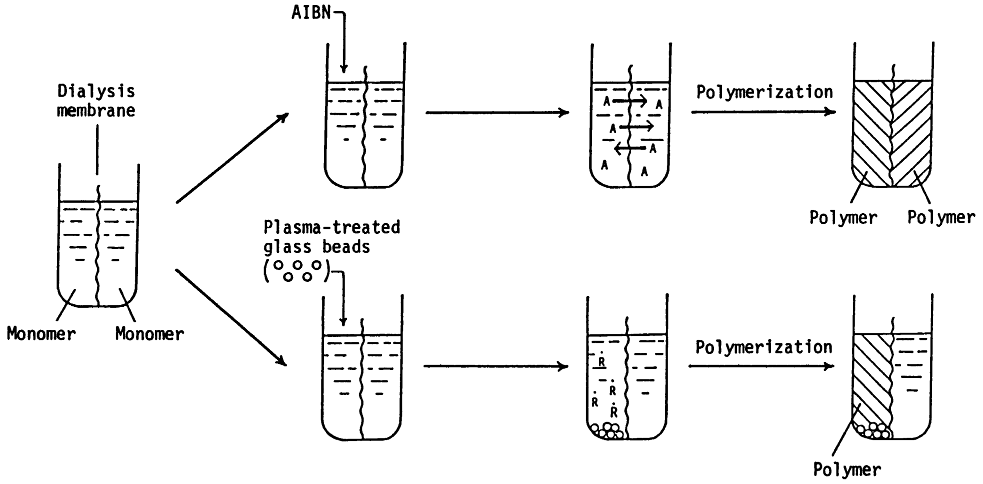

Fig. 1. Schematic representation for polymerization of AA through dialysis membrane.

With this thought in mind, we have carried out 50% aqueous solution polymerization of AA at 65°, according to the method shown in Fig. 1, using two kinds of dialysis membranes of MWCO 1000 and MWCO 12000-14000 (Spectra/Por dialysis tubing, Spectrum Medical Ind. Ltd.) in a 50 mL ampule, by placing the prescribed quantities of glass beads (2.7-3.0 mm diameter) in only one of the two monomer layers, which were previously treated with a brief plasmolysis of various organic vapors such as methyl isobutyrate (MIB), 1,5-hexadiene (HD) and benzene.[9)]

Table 1. Effect of permeability of the radicals leached out of the ultrathin film through dialysis membrane on aqueous solution-polymerization of AA

Organic vapor for plasmolysis	Layer	Dialysis membrane (A) M.W. cutoff:1000			Dialysis membrane (B) M.W. cutoff:12000-14000		
		Propagation period/h	Yield/%	R_p/M l^{-1} s^{-1}	Propagation period/h	Yield/%	R_p/M l^{-1} s^{-1}
MIB	inner	0.5	7.04	2.72×10^{-4}	0.6	6.69	2.21×10^{-4}
	outer		trace	≈ 0		5.25	1.73×10^{-4}
HD	inner	1.0	9.26	1.79×10^{-4}	0.5	2.89	1.11×10^{-4}
	outer		1.01	1.95×10^{-5}		1.83	7.06×10^{-5}
Benzene	inner	1.0	8.76	1.69×10^{-4}	0.75	4.38	1.12×10^{-4}
	outer		1.95	3.76×10^{-5}		2.03	5.22×10^{-5}

The results were summarized in Table 1. It is clearly seen from Table 1 that the polymerizations of AA of the inner layer (in the presence of plasma-exposed glass beads) proceeded more efficiently than those of the outer layer (in the absence of plasma-treated glass beads) in both cases of the dialysis membrane for molecular weight cutoff 1000(A) and 12000-14000(B). We believe this difference in efficiency of the polymerization between the two layers stems from the consequence that the active radicals to initiate the polymerization of AA are of high molecular weight so that they are restricted to permeate through the dialysis membrane. Another interesting feature of this result is that the same difference is far more greater for the case of the former membrane (A), and the polymerization of the outer layer induced by MIB plasma-driven ultrathin film was scarcely effected, indicating that the active radicals of the molecular weight of less than 1000 are almost non-existent in this case. Further, the difference in the polymerization rate of the outer layer between the two kinds of dialysis membranes, A and B, indicated the presence of radicals distributed over a wide range of molecular weight.

Recently we have also shown that the aqueous solution obtained from agitation in various organic plasma-exposed glass ampules followed by pouring it into a new ampule can also induce the polymerization of AA, demonstrating that active radicals are also slowly generated in such a solution.10) Based on this fact, it can be considered that the following process for the radical generation has also been included; a fragmented piece of film has first been peeled off into a solution, from which active radicals are consecutively generated in the solution over a long period of time. This process would also contribute to the difference in the polymerization rate of the outer layer between the two kinds of dialysis membranes, A and B.

The present results as well as those previously studied by the BNB spin trapping techniques provided useful information concerning not only structural features of radicals leached out of the film but also those of the resulting polymer in the polymerization initiated by the plasma-driven ultrathin film.

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