MECHANOCHEMICAL REACTIONS OF PLASMA-INDUCED SURFACE RADICALS ON POLYETHYLENE

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It is a well known fact that plasma-irradiation of inert gas creates effectively free radicals on polymer surface. These surface radicals permit reactions for surface modifications in several different ways such as CASING, graft polymerization and introduction of functional groups (plasma treatment). However, the characterization of such plasma-induced surface radicals and their reactivities have not been worked out. Thus, we have reported the detailed electron spin resonance (ESR) studies of plasma-induced surface radicals of a variety of synthetic and natural polymers with the aid of systematic computer simulations.[1-12] All kinds of organic radicals eventually undergo a termination reaction, producing stable molecules. The paths available to a pair of radicals are recombination and disproportionation. Unlike radicals in the liquid or gas phase, however, the recombination of solid state radicals is significantly suppressed due to the restriction of their mobilities. Interaction between radicals at solid-solid interfaces do not occur under a normal condition.

From these points of view, our interest was focused on the possible occurrence of solid state radical recombination on plasma-irradiated polymeric powders, resulting from application of mechanical energy such as vibratory milling before the surface radicals could undergo the usual reactions to give stable diamagnetic molecule.

It is known that mechanical fracture of polymers at the temperature lower than the glass transition point (T_g) causes the mechano-radical formation due to polymer mainchain scission. Thus, we have selected for an initial study a plas-

ma-irradiated high density polyethylene (PE), since the T_g of PE is lower than room temperature (around $-80 \sim -90^\circ\text{C}$) so that radicals are not mechanically formed at room temperature.

We report the experimental evidence of facile solid state radical recombination reactions induced by application of mechanical energy based on the observation of ESR spectra.

Vibratory milling of PE (100 mg) plasma-irradiated for 10 min (ICP at 13.56 MHz with 40 W, Ar; 0.5 Torr) was conducted with a Teflon-made ball (6 mm diameter, 288 mg) in a Teflon twin-shell blender (7.8 mm diameter, 24 mm long) at room temperature under strictly anaerobic conditions. We have used a Teflon-made vessel for mechanical vibration in the present study to eliminate any possibility of unnecessary side reactions such as mechanically-induced solid state single electron transfer (SSET) reaction in the case of metallic vessel.[13-15]

Figure 1 shows progressive changes of the observed ESR spectra (A) of plasma-irradiated PE on the vibratory milling together with the corresponding simulated spectra (B). It is clear from Figure 1A that the spectral intensity gradually decreased with change of the spectral pattern as the duration of vibratory milling increased. Thus, the application of mechanical vibration appears to cause the effective decay in the PE radical concentration, since the radicals do not dissipate appreciably on standing at room temperature. It also appears based on the progressive changes of the spectral pattern during the period of mechanical vibration that the mechanical reactivity varies with the structure of the radicals, since plasma-irradiated PE consists of three kinds of radicals, midchain alkyl radical (sextet spectrum), allylic radical (septet spectrum) and dangling bond sites (DBS) (smeared-out broad line spectrum) as reported earlier.[9]

The progressive changes of the spectral intensity determined by the double integration of ESR as a function of duration of mechanical vibration under various vibratory milling conditions are shown in Figure 2. It is seen that the decrease in the spectral intensity depends on the frequency of the vibratory milling which corresponds to the applied mechanical energy. The surface radicals decay with a faster rate as the applied mechanical energy increases under otherwise identical conditions. Figure 3 shows the nature of decay of the spectral intensity of the component radicals deduced from the simulated spectra. It can be

Fig.1 Progressive changes of observed(A) and simulated ESR spectra(B) of plasma-irradiated PE powders with various duration of vibratory milling(17Hz) .

Fig.2 Progressive changes in spectral intensity of PE radical under various vibratory milling conditions. Mill vibration frequency: ●;0Hz, ○;10 Hz, ◐;17Hz, ◑;20Hz, ◒;30Hz.

Fig.3 Progressive changes in spectral intensity of component radicals: ●;total, ⊙;sextet, ◐;septet, ◑;DBS.

seen that the sextet spectrum of the midchain alkyl radical decays with much a faster rate than the other two component spectra of allylic radical and DBS, whose decays are negligible at least within duration for 60 min vibration.

Note that the decay curve of the sextet spectrum was well fitted with the second-order kinetics, indicating that the dissipation of the midchain alkyl radical follows a bimolecular reaction.

It is hoped that more precise nature of solid state radical recombination reactions will be gained in the course of attempts now in progress to explore such reactions in various other types of plasma-irradiated polymers.

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