Nature of Auto-Oxidations on Plasma-Induced Surface Radicals of Aromatic Ring-Containing Polymers as Studied by Electron Spin Resonance

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Peroxy radical formation as an initial reaction for auto-oxidation process has been extensively studied due to importance of industrial application of a wide variety of irradiated-polymers. All kinds of plasma-irradiated polymers are eventually exposed to air for their practical use, so that the studies of auto-oxidation process are also important for understanding the nature of plasma treatment. In a previous paper, we reported the special features of the peroxy radicals formed from plasma-irradiated polyethylene, high density and low density, as studied by electron spin resonance (ESR). In this paper, we report the first ESR study on the peroxy radical formation of plasma-irradiated aromatic ring-containing polymers such as polycarbonate (PC), polyethyleneterephthalate (PET) and polyimide (PI) shown in Fig. 1 by its exposure to air (oxygen) after Ar plasma-irradiation.

The progressive changes of room temperature ESR spectra of Ar plasma-irradiated polymer powders of PC, PET and PI with various plasma durations are shown in Fig. 2, together with the corresponding simulated spectra shown as dotted lines. It can be seen that even less than several seconds of plasma duration gave enough amount of radicals to such an extent as can be detected by conventional ESR measurements, and all the spectral intensities increase as the plasma duration increases. It is also seen that each spectral pattern in PC and PET gradually changed, which is characterized by a relative decrease in the lateral peaks on the outer side of both the higher and lower field of the major central peaks, whereas that of PI did not appreciably change even on prolonged irradiation.

Fig. 1. Structures of aromatic-containing polymers, PC, PET and PI.
In view of the fact that surface reactions of plasma treatment are initiated by plasma-induced surface radicals, we reported a detailed ESR study on plasma-induced radicals of a variety of polymers, synthetic and natural, including aromatic ring-containing polymers. From a series of such studies, we have already shown that the observed ESR spectra of two polymers, PC and PET, were deconvoluted with the aid of the systematic computer simulations invoking essentially two types of component spectra as a common feature, one derived from a cyclohexadienyl-type radical (formed by a hydrogen atom addition to the benzene ring) and a single broad line spectrum derived from dangling bond sites (DBS) at the surface cross-linked region. It should be noted that the spectral intensity of PI is much larger than two other spectra and the spectrum consists of a single component. This fact was very intriguing because PI possesses no abstractable hydrogen attached to SP³ carbon, so that it can be considered that the radical formation should be the least among three polymers examined. This paradox was found to be explained in terms of the fact that all the commercially available PIs always contain a small amount of dimethylformamide (DMF) used as a solvent on their preparation and can not be completely eliminated (based on the result of NMR spectral measurements). Thus, we assigned likewise the observed single line spectrum to DBS formed by complex reactions of PI and contaminated DMF. We also note that the cyclohexadienyl-type radicals are quite rapidly formed in any aromatic ring-containing polymers but are thermally much less stable and have a great tendency to undergo the radical recombination reactions leading to the formation of thermally stable DBS during the course of prolonged plasma irradiation. Thus, the cyclohexadienyl-type radical was a major component in earlier spectra of Fig. 2, but the relative ratio of DBS gradually increased and became a major component as plasma duration increased, and on anaerobic standing of plasma-irradiated sample at room temperature.

In the light of these facts, we have studied the nature of peroxy radical formation on two types of polymer samples plasma-irradiated for 3 s and plasma-irradiated for 180 s followed by prolonged standing at room temperature under anaerobic conditions.

The formation of the corresponding peroxy radical was furnished by opening the ample containing Ar plasma-irradiated polymer samples to introduce an dry air into the ample. After agitating the powder samples, the ESR spectra were periodically measured according to the same method as reported previously.

Figure 3 shows what happened to the ESR spectra when three polymer samples plasma-irradiated for 3 s was exposed to air immediately after Ar plasma irradiation.
It is seen that exposure to air has caused a very rapid dissipation of the radicals in all cases, although a small amount of lower-reactive DBS was observed in PI, indicating the occurrence of facile reactions of the radicals with oxygen resulting in the formation of non-radical species. The result is in sharp contrast to that of many other non-aromatic ring-containing polymers where they give a typical g-anisotropic spectra of peroxy radicals observable for an appreciable period of time at room temperature. This specificity can be ascribed to an occurrence of a hydrogen subtraction by oxygen from cyclohexadienyl-type radical to reconvert to the original aromatic compound in PC and PET. This type of reaction is long known in aromatic ring-derived radicals of various kinds of aromatic compounds.

On the other hand, Figure 4 shows what happened to the ESR spectra when three polymer samples plasma-irradiated for 180 s followed by prolonged standing containing DBS as a major component was exposed to air.

As can be seen from Fig. 4, the spectra were observed in all three polymers ($I_{\text{min}} / I_0 = $ ca. 0.93 for PC, ca. 0.38 for PET, and 0.19 for PI), unlike those in Fig. 3, although the spectral intensities gradually decreased on standing at room temperature. The spectra of PC and PI are found to be all carbon-centered radicals based on the g-value, so that they can be ascribed to low reactive DBS located at the inner surface layer, and the corresponding peroxy radicals must have dissipated rapidly.

While the observed spectrum of PET disappeared within 1 h and found to be a peroxy radical derived from DBS based on the larger g-value. This result indicated that PET does not produce low reactive DBS so that it is considered PET is the least crosslinkable polymers among three polymers.

It has been reported that the effect of plasma treatment on introducing the surface hydrophilicity is less effective and/or complicated in aromatic ring-containing polycondensed polymers than many other types of polymers without a detailed explanation. This may be interpretable from the present study in terms that cyclohexadienyl-type radicals rapidly formed in a shorter plasma duration merely revert to aromatic ring on reaction with oxygen instead of incorporation of oxygen functional groups, while the formation of DBS became predominant on longer plasma duration, indicating the hydrophobic crosslinked surface are gradually formed.

In general, aromatic ring-containing polycondensed polymers are of bifunctionality in plasma irradiation effect, degradable and crosslinkable at aromatic rings and degradable at oxygen-containing ester groups. So it is especially important to choose the plasma operational conditions for producing two types of radicals with appropriate ratio for effective plasma treatment.

If plasma irradiated polymers contains mainly cyclohexadienyl-type radicals, oxygen functional groups would not be effectively incorporated, although intense ESR spectral peaks were observed, while if such polymers contain a large amount of DBS, it should be considered that the polymer is of crosslinked surface and introduction of oxygen functional groups are suppressed.

From the present studies on auto-oxidation processes of various kinds of aromatic ring-containing polycondensed polymers, it can be

Fig. 4. Progressive ESR spectral changes on exposure to air of several aromatic-containing polymers Ar plasma-irradiated for 3 min followed by standing for 10 days, together with the simulated spectra shown as dotted lines.
concluded that it is very important to select the plasma operational conditions to achieve the effective plasma treatment.

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