

## Electron Spin Resonance Studies on Graft Copolymerization of Gaseous Styrene onto Preirradiated Polypropylene. III. Preirradiation Under Vacuum Followed by Exposure to Oxygen at $-78^{\circ}\text{C}$

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### Synopsis

Grafting of styrene vapor was carried out onto polypropylene  $\gamma$ -irradiated under vacuum followed by exposure to oxygen at  $-78^{\circ}\text{C}$ . A comparison with the results on polypropylene irradiated in an oxygen atmosphere leads to an interesting result. Two samples were irradiated at room temperature under vacuum and in an oxygen atmosphere, respectively, the former being followed by exposure to oxygen. Although irradiation was carried out at room temperature for either sample and nearly the same amounts of the peroxy radicals are trapped, the former showed more grafting than the latter. The origin of this difference was investigated by means of electron spin resonance. Significant differences were observed in ESR spectra as well as in isothermal decays of the trapped peroxy radicals. In the former sample, the trapped peroxy radicals had a higher mobility, and consequently a significant hydrogen abstraction by the peroxy radicals was observed during storage at  $40^{\circ}\text{C}$ . This result supports the conclusion of the previous paper that the radicals effective in the grafting reaction of polypropylene preirradiated in an oxygen atmosphere are the carbon radicals which are produced by hydrogen abstraction by the peroxy radicals.

### INTRODUCTION

As reported before, graft initiation activities of preirradiated polypropylene differ with irradiation conditions.<sup>1,2</sup> In oxygen atmosphere,<sup>1</sup> preirradiation at  $-78^{\circ}\text{C}$  resulted in more grafting than irradiation at room temperature. This was explained by the fact that the peroxy radicals trapped in the amorphous region at low temperature are able to abstract hydrogen atoms from the neighboring polymer chains to form the carbon radicals which are the active centers of the graft initiation. On the other hand, preirradiation under vacuum<sup>2</sup> showed little difference of grafting between  $-78^{\circ}\text{C}$  and room temperature. This is so because the carbon radicals trapped in the amorphous region are too unstable to be involved in the grafting reaction. As reported previously,<sup>3</sup> irradiation under vacuum at room temperature followed by exposure to oxygen at  $-78^{\circ}\text{C}$

produces peroxy radicals with higher mobility than those produced by room-temperature irradiation in an oxygen atmosphere. We studied, therefore, the grafting reaction initiated by the peroxy radicals under this condition. As a result, additional confirmation on the conclusion in our previous papers is obtained.

### EXPERIMENTAL

Materials, irradiation, ESR measurement, and the procedure of grafting reaction are the same as those described in the previous papers.<sup>1,2</sup> Polymer samples were degassed at about  $10^{-5}$  torr for 24 hr before irradiation. After irradiation at  $-78^{\circ}\text{C}$  or at room temperature, oxygen was introduced at  $-78^{\circ}\text{C}$  by breaking a seal attached to the sample tube containing polymers. After introduction of oxygen, samples were kept at  $-78^{\circ}\text{C}$  for 24 hr to complete the reaction of the carbon radicals with oxygen and then were degassed before ESR measurement or grafting reaction. The reaction temperature with oxygen was chosen to avoid the decay of the trapped radicals.

For convenience, the two kinds of samples, the polymers irradiated at  $-78^{\circ}\text{C}$  and at room temperature under vacuum followed by exposure to oxygen, are denoted by sample D and sample R, respectively.

### RESULTS AND DISCUSSION

#### Grafting Yield

In Figure 1, the grafting yields expressed by the percentage grafting of samples D and R are plotted against the storage time at  $40^{\circ}\text{C}$  in styrene vapor. Contrary to results in polymers irradiated in an oxygen atmosphere, a significant difference in grafting yield between samples D and R was not found. For example, the grafting yields after 16 hr are 34% and 36% for samples D and R, respectively. Such small differences in grafting were found also in the reactions initiated by the carbon radicals.<sup>2</sup> It is especially interesting that sample R gives a much higher grafting yield

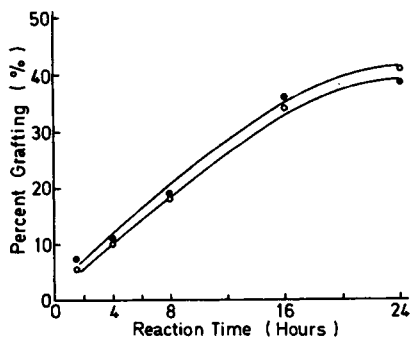


Fig. 1. Grafting of gaseous styrene onto preirradiated polypropylene: (O) sample D; (●) sample R; reaction temperature,  $40^{\circ}\text{C}$ .

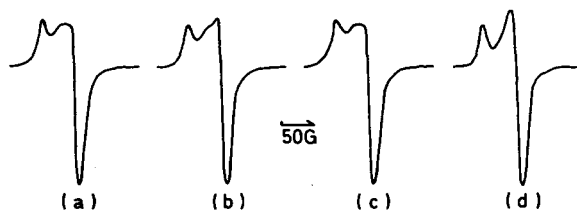


Fig. 2. ESR spectra of the peroxy radicals of polypropylene: (a) sample D; (b) sample R; (c) sample irradiated at  $-78^{\circ}\text{C}$  in oxygen atmosphere; (d) sample irradiated at room temperature in oxygen atmosphere.

than polymers irradiated at room temperature in an oxygen atmosphere. In order to understand the origin of this difference, ESR spectra of these peroxy radicals were measured.

### ESR Spectra

Figures 2a and 2b show the ESR spectra of the peroxy radicals produced in samples D and R, respectively. Although the two samples are irradiated at different temperatures, the spectra are quite similar. The spectrum of sample D is the same as that of the peroxy radicals produced by irradiation at  $-78^{\circ}\text{C}$  in an oxygen atmosphere (Fig. 2c). On the other hand, the spectrum of sample R is not the same as that of the peroxy radicals produced by room-temperature irradiation in an oxygen atmosphere (Fig. 2d), although irradiation was carried out at room temperature in both cases. The spectral difference arises from the superposition of a broad component which was also found in the peroxy radicals produced by irradiation at  $-78^{\circ}\text{C}$  in an oxygen atmosphere. The temperature dependence of this broad component was found to be quite similar to that of the peroxy radicals produced by the low-temperature irradiation. As has been already discussed by us,<sup>1,3</sup> it is suggested that some of the peroxy radicals are trapped in a less rigid matrix in which the radicals have more mobility. Our previous work shows that carbon radicals are not trapped in an amorphous region when the irradiation is carried out at room temperature. It appears, then, that the peroxy radicals are trapped in a less rigid matrix, in which their precursors have not been trapped before the reaction with oxygen. If some of the peroxy radicals are trapped in a less rigid matrix, as suggested by ESR spectra, their isothermal decay should be similar to that of sample D or the peroxy radicals produced by irradiation at  $-78^{\circ}\text{C}$  in an oxygen atmosphere. To examine this, the isothermal decay of radicals was measured at  $40^{\circ}\text{C}$ .

### Amounts of Trapped Radicals and Isothermal Decay

The isothermal decay of radicals at  $40^{\circ}\text{C}$  under vacuum was measured in the same manner as in the previous papers.<sup>1,2</sup> The result is shown in Figure 3. Since the same standard  $\text{Mn}^{2+}$  sample was used also in the present work for the determination of amounts of the trapped radicals, it is

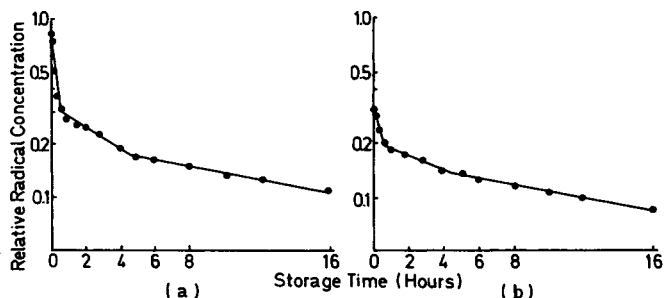


Fig. 3. Isothermal decay of peroxy radicals at 40°C: (a) sample D; (b) sample R.

possible to compare the relative concentrations directly with those reported in the previous papers.<sup>1-3</sup> Sample D shows the three-step decay which is just the same as that of the peroxy radicals produced by irradiation at  $-78^{\circ}\text{C}$  in an oxygen atmosphere. Sample R also shows a similar three-step decay, as expected. It was found in our previous work<sup>1,3</sup> that the peroxy radicals produced by the room-temperature irradiation in an oxygen atmosphere exhibit only the last two steps of decay and that the first step is due to the radicals trapped in an amorphous region. Therefore, it is suggested that some of the peroxy radicals in sample R are trapped in a less rigid matrix. These peroxy radicals are expected to abstract hydrogen from the polymer chain just as peroxy radicals produced in polymers irradiated at  $-78^{\circ}\text{C}$  in an oxygen atmosphere.

### Hydrogen Abstraction

Figure 4 shows the ESR spectra of samples D and R which are measured after annealing for 4 hr at 40°C under vacuum. Both spectra show that considerable amounts of the carbon radicals are produced by hydrogen abstraction. The peroxy radicals produced by the room-temperature irradiation in oxygen atmosphere did not show such a hydrogen abstraction at 40°C for at least 10 hr. It is to be noted that similarities between samples D and R are found not only in the three-step decay but also in hydrogen abstraction. Apparently such similarities seem curious because hydrogen abstraction is to be caused by the peroxy radicals trapped in the amorphous region in which sample R does not contain any carbon radicals before the reaction with oxygen.

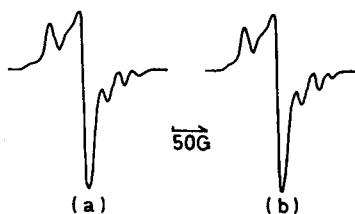


Fig. 4. ESR spectra of polypropylene measured at  $-78^{\circ}\text{C}$  after annealing at 40°C under vacuum for 4 hr: (a) sample D; (b) sample R.

However, the results may be understood if it is assumed that radical-site migration takes place. As mentioned above, the peroxy radicals are able to abstract hydrogen atoms easily in an amorphous region. If the carbon radicals remained in an amorphous region as they were, they would decay out during the first step of decay. The fact that the carbon radicals are found after the decay of radicals in an amorphous region suggests that the carbon radicals are stabilized in the nonamorphous region as a result of radical-site migration.

On the other hand, the migration from a nonamorphous to an amorphous region will also occur. Such a radical-site migration along polymer chains has been reported to take place as a result of intramolecular proton transfer.<sup>4-6</sup> When oxygen is introduced to sample R, oxygen diffuses into an amorphous region more easily than into a nonamorphous region. In a boundary region, therefore, oxygen reacts with the carbon radicals which migrated along polymer chains from a nonamorphous region, and the peroxy radicals are trapped there. Upon being converted to the peroxy radicals, they are unable to migrate along the polymer chains. Consequently, considerable amounts of peroxy radicals are found in the less rigid matrix in sample R, and they abstract hydrogen atoms to form the carbon radicals which become graft initiation centers. In the previous paper,<sup>1</sup> it was concluded that the carbon radicals produced by hydrogen abstraction of the peroxy radicals trapped in an amorphous region are the grafting active centers. The results obtained in the present work confirm this conclusion.

## CONCLUSIONS

Sample R shows the grafting activity comparable to that of sample D. Part of the peroxy radicals in sample R are trapped in a less rigid matrix, as shown both in their ESR spectra and in their decay behavior. Consequently, they are able to abstract hydrogen atom from the neighboring polymer chains to form the carbon radicals in this matrix. These results confirm the conclusion of the previous papers that the carbon radicals thus formed are the active centers of the grafting reaction.

## References

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