

Electron Spin Resonance Studies on Graft Copolymerization of Gaseous Styrene onto Preirradiated Polypropylene. II. Preirradiation Under Vacuum

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Synopsis

Graft copolymerization of gaseous styrene was carried out at 40°C onto polypropylene preirradiated under vacuum. In order to investigate the origin of graft initiation activity, ESR spectra of irradiated polymers were measured and discussed. Although there are about three times as many radicals trapped in the sample irradiated at -78°C as in the sample irradiated at room temperature, both the samples showed nearly same degree of grafting. This is due to the ineffectiveness of radicals trapped in the amorphous region for grafting. The samples irradiated under vacuum showed more grafting than those irradiated in an oxygen atmosphere. This is compatible with the conclusion in the previous paper that in grafting of polypropylene irradiated in an oxygen atmosphere the carbon radicals produced by hydrogen abstraction by trapped peroxy radicals are the effective active centers.

INTRODUCTION

Grafting of gaseous styrene onto polypropylene preirradiated in an oxygen atmosphere was studied in our previous work,¹ in which it was concluded that the radicals having graft initiation activities are not the trapped peroxy radicals but the carbon radicals produced by hydrogen abstraction by peroxy radicals. It is interesting to compare these results with those for polymers preirradiated under vacuum, since carbon radicals are produced and trapped in the latter sample.

In the present work, grafting of styrene vapor onto polypropylene preirradiated under vacuum was carried out. Since it was found that the irradiation temperature seriously affects the degree of grafting in the case of preirradiation in an oxygen atmosphere, the effect of irradiation temperature was investigated on electron spin resonance (ESR) spectra as well as on the graft activity of the trapped radicals. There was a large difference in the amount of trapped radicals in addition to qualitative differences in ESR spectra as well as in the decay behavior between two samples irradiated at -78°C and at room temperature, respectively. However, little

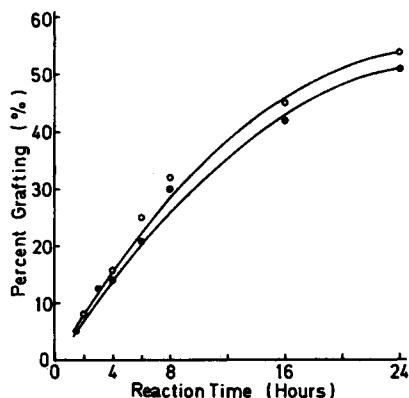


Fig. 1. Grafting of gaseous styrene onto preirradiated polypropylene: dose, 3×10^6 rad, reaction temperature, 40°C ; irradiation temperature, (○) -78°C ; (●) room temperature.

difference in degree of grafting was found between them. In the present paper, the graft initiation activity of polymers preirradiated under vacuum is discussed in relation to the results for the preirradiation in an oxygen atmosphere.

EXPERIMENTAL

Materials, the irradiation source, the procedure of grafting reaction, and the ESR measurement are the same as in the previous paper,¹ except that irradiation was carried out under vacuum. Polymer samples were degassed at about 10^{-5} torr for 24 hr before irradiation. The degree of grafting was expressed as a per cent increase in weight.

For the determination of relative radical concentrations by ESR, the same Mn^{2+} standard sample was used under the same condition as in the previous paper.¹

RESULTS AND DISCUSSION

Degree of Grafting

The degree of grafting of styrene onto polypropylene preirradiated under vacuum is shown in Figure 1. The abscissa of this figure represents the storage time at 40°C after breaking a seal which is situated between the polymer sample and monomer reservoir. Compared with results for irradiation in an oxygen atmosphere, the effect of irradiation temperature is less pronounced. It is to be noted that more grafting is found for polymers irradiated under vacuum than for polymers irradiated in an oxygen atmosphere. For example, the degrees of grafting at 16 hr after the introduction of styrene vapor are 45% and 42% for the polymers irradiated under vacuum at -78°C and at room temperature, respectively. These are to be compared with 23% and 7% for polymers irradiated in an oxygen atmo-

sphere at -78°C and at room temperature, respectively.¹ In order to elucidate the reason why the irradiation temperature did not affect the degree of grafting in contrast to irradiation in an oxygen atmosphere, ESR spectra of the trapped radicals and their decay behavior were examined.

ESR Spectra of Trapped Radicals

ESR spectra of polypropylene irradiated under vacuum have been studied by a number of workers.²⁻¹⁰ The spectra obtained by irradiations at -196°C and at room temperature were initially attributed to the alkyl and the allyl radicals, respectively, by Fischer and Hellwege.⁴ The spectrum observed at room temperature, which consists of 20 lines, changed reversibly to a 9-line spectrum when measured at -196°C .^{4,10} This spectrum was reinterpreted by Ayscough and Munari⁹ to be assigned to the alkyl radical. It was pointed out by one of the authors and his co-workers that the spectrum obtained by irradiation at -196°C consists of 9-line and 4-line components, the latter being probably due to the radical $-\text{CH}_2-\text{CH}(\dot{\text{C}}\text{H}_2)-\text{CH}_2-$.¹⁰ A confirmation for the interpretation by Ayscough and Munari was obtained by the reversible radical conversion induced photochemically and thermally.

The spectra obtained by irradiation at -78°C and at room temperature are shown in Figure 2. Both spectra were measured at -78°C . Figure 2b shows a 9-line hyperfine structure similar to that measured at -196°C , while Figure 2a obtained by irradiation at -78°C has an appreciable 4-line component. It is to be noted that the hyperfine line width of the spectrum shown in Figure 2a is broader than that in Figure 2b. The difference between these two spectra will be characterized in the course of the study on the isothermal decay of radicals.

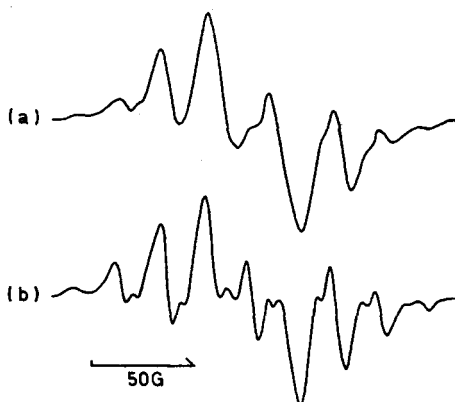


Fig. 2. ESR spectra of polypropylene irradiated under vacuum: irradiation, (a) at -78°C ; (b) at room temperature; measurement at -78°C .

Amounts of Trapped Radicals and Decay Under Vacuum

Figure 3 shows a first-order plot of the isothermal decay of trapped radicals at 40°C under vacuum. The initial concentration of the trapped radicals is higher in the sample irradiated at -78°C than in that irradiated at room temperature, just as in the case of the peroxy radicals in the previous paper.¹ Furthermore, the decay curves are quite similar to those of the peroxy radicals. Since the same standard sample as that in the previous paper is used for the measurements of relative radical concentrations, it is obvious that nearly equal concentrations of radicals are trapped in both the samples irradiated in an oxygen atmosphere and under vacuum. This is natural when it is assumed that the carbon radicals produced by irradiation under vacuum are the precursors converted quantitatively to the peroxy radicals.

For the sample irradiated at -78°C, three steps of decay were found, while only two steps corresponding to the second and the third steps in the sample irradiated at -78°C were found for the sample irradiated at room temperature as is the case of the peroxy radicals. It is obvious that the difference in total amount of radicals between the samples irradiated at -78°C and at room temperature is due to the existence of the radicals which show the first step of rapid decay in the sample irradiated at -78°C. The fact that the carbon radicals exhibit nearly the same decay curves as the peroxy radicals suggests that the decay rate of radicals is dependent mainly on the rigidity of the matrix in which the radicals are trapped.

In order to confirm this, the decay was measured on two kinds of polypropylene film of different crystallinity. One film was obtained by quenching from 135°C to 0°C, and the other was obtained by annealing for 24 hr at 135°C followed by slow cooling. These two films were γ -irradiated at -78°C, and the isothermal decays of radicals were measured at 40°C. The results are shown in Figure 4. Although the total amounts of radicals initially trapped in the films are not very different from each other, the proportion of the radicals which show a rapid decay of the first step was larger in the former film as expected.

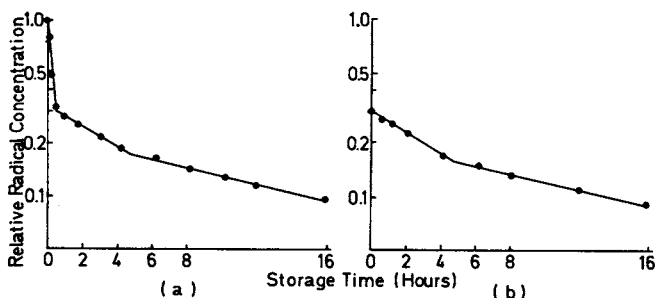


Fig. 3. Isothermal decay of the carbon radicals at 40°C: (a) powders irradiated at -78°C; (b) powders irradiated at room temperature.

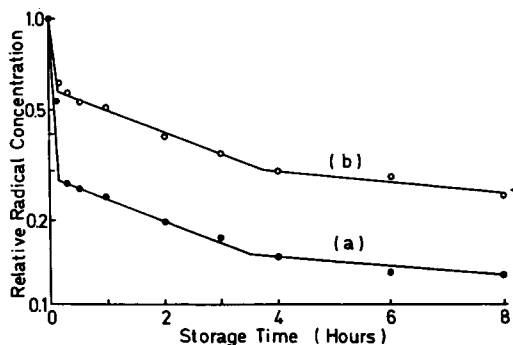


Fig. 4. Isothermal decay of carbon radicals trapped in polypropylene irradiated at -78°C : (a) film quenched from 135°C to 0°C ; (b) film annealed at 135°C .

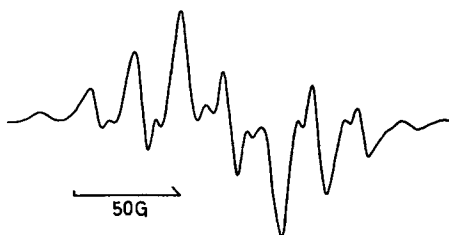


Fig. 5. ESR spectrum of polypropylene irradiated at -78°C : measured at -78°C after annealing at 40°C under vacuum for 1 hr.

During storage at 40°C of the sample irradiated at -78°C , the decrease of the spectral intensity was accompanied by a change of the line shape, e.g., the spectrum of Figure 2a changed to one shown in Figure 5 after 1 hr. The spectral subtraction of Figure 5 from Figure 2a shows that the 4-line component has disappeared. The amount of the 4-line component is estimated to be about 40% from the decomposition of the initial spectrum (Fig. 2a) into the 4- and 9-line components. However, the amount of radicals which disappeared in the first step of rapid decay is about 70%. Evidently this exceeds the amount of the 4-line component. Therefore, some of the 9-line component also decayed in the first step of decay. In fact, the subtraction of the spectrum measured at the end of the first step of rapid decay from the initial spectrum shows the 9-line component together with the 4-line component. The broader line width in the spectrum of the low-temperature specimen is attributed to this unstable 9-line component.

These unstable 9-line and 4-line components are, therefore, ascribed to the radicals trapped in a region of less rigid matrix, e.g., an amorphous region. After the first rapid decay of radicals, the 4-line component is not found. This does not mean that the radicals corresponding to the 4-line component are not trapped in more rigid matrices. It is rather reasonable to suppose that in more rigid matrices, the radicals giving the 4-line spectrum have been converted to the radicals responsible for the 9-line spectrum during the storage at 40°C .¹⁰

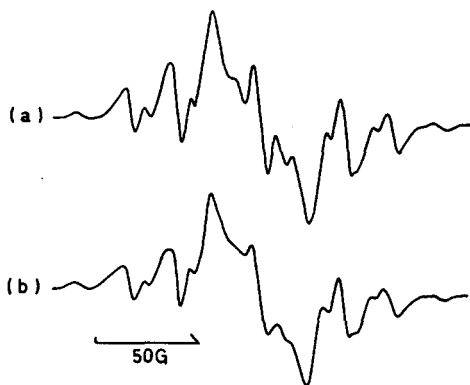


Fig. 6. ESR spectra of polypropylene irradiated at -78°C : measured at -78°C after annealing at 40°C under vacuum for (a) 3 hr and (b) 6 hr.

The spectra measured in the second and the third steps of decay are shown in Figure 6. The broad spectrum, which becomes conspicuous with storage time, is observed in the central part of the 9-line spectrum. Owing to its unresolved hyperfine structure, this broad spectrum is difficult to interpret, but it is perhaps the radical species which Fischer and Hellwege⁴ assigned to the polyenyl radical and Ayscough and Munari⁹ reassigned to the allyl radical. The latter interpretation seems more probable.

Spectral Change and Decay in the Styrene Vapor

The isothermal decay of the carbon radicals at 40°C in the styrene vapor was also measured. Although there was no noticeable difference in radical decay in the styrene vapor and under vacuum, a difference was found in the spectra. Figure 7 shows the spectrum after storage at 40°C in styrene vapor for 6 hr. The broad component observed in the central part of Figure 6b is not seen in Figure 7. This may suggest that the active center effective in grafting is the allyl radical responsible for the broad component. For the present, however, it is difficult to decide whether styrene reacted with the allyl radicals or whether it depressed the conversion from the alkyl to the allyl radicals.

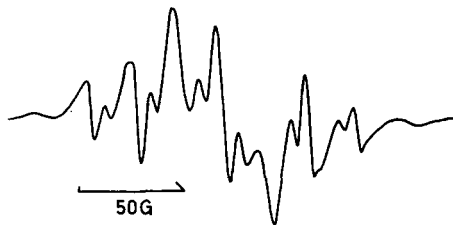


Fig. 7. ESR spectrum of polypropylene irradiated at -78°C : measured at -78°C after annealing at 40°C in styrene vapor for 6 hr.

Grafting Activity

As mentioned above, the difference in grafting yield is not pronounced between samples irradiated at -78°C and at room temperature, although the amounts of the trapped radicals are quite different. This suggests that the radicals showing the rapid decay in polymers irradiated at -78°C are not effective in the grafting reaction. This was confirmed also by introducing the styrene vapor after the polymer sample irradiated at -78°C had been annealed for 1 hr at 40°C to eliminate the radicals which show the first step of rapid decay. Whether the styrene vapor was introduced just after irradiation or after annealing for 1 hr, no significant difference was found in the graft yield. It is obvious that the radicals showing slower two-step decay are involved in the grafting reaction.

CONCLUSION

The percentage grafting was similar in polymers irradiated under vacuum at -78°C and at room temperature. This indicates that the carbon radicals trapped in the amorphous region are not effective in the grafting reaction. In the case of the irradiation in an oxygen atmosphere, it was suggested that the radicals which are very effective in the grafting reaction are not the trapped peroxy radicals themselves but the carbon radicals produced by hydrogen abstraction by the peroxy radicals trapped in the amorphous region. This is compatible with the fact that more grafting was obtained in the case of the carbon radicals of polymers irradiated under vacuum.

It is concluded that low-temperature irradiation in an oxygen atmosphere favors the trapping of radicals in the amorphous region in which the hydrogen abstraction reaction is easier, producing a more effective graft-initiating center, the carbon radical, while the low-temperature irradiation under vacuum does not have any advantage because of the low activity of carbon radicals trapped in the amorphous region.

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