

Radiation-Induced Graft Copolymerization of Butadiene on Polyethylene by Trapped Radicals

AKIRA FURUHASHI,* HIROSHI MUKOZAKA, and HIROSHI MATSUO, *Ibaraki Annex, Electrical Communication Laboratory, Nippon Telegraph and Telephone Public Corporation, Tokai-Mura, Ibaraki, Japan*

Synopsis

The low-temperature grafting of butadiene on polyethylene (PE) preirradiated in air is compared with that on PE preirradiated *in vacuo* for the effect of several factors on the grafting. Little fundamental difference between the two cases was observed. In both cases the graft conversion curve is trapped radical type and the overall activation energies are 9.7 and 8.4 kcal/mol for 0.947-density PE and 0.916-density PE, respectively. Percent grafting is proportional to the square root of the dose rate (= total dose). The retarding effect of oxygen at irradiation or storage after irradiation on the grafting scarcely appears when the irradiation temperature or storage temperature is below 15°C. For thinner film and lower density of PE this effect appears clearly at the higher temperature. Therefore, it may be concluded that the low-temperature grafting of butadiene onto PE preirradiated in air is initiated predominantly by nonoxidized radical (allyl radical) trapped in PE and that the grafting reaction occurs in the semicrystalline part of PE.

INTRODUCTION

There are many reports on graft copolymerization by trapped radicals in preirradiated polyethylene.¹ In the case of polyethylene (PE) preirradiated *in vacuo* Ballantine et al.² have reported that the trapped radicals are able to induce graft copolymerization, and Tamura et al.^{3,4} have estimated in the case of PE-styrene graft copolymerization that the grafting is due almost entirely to trapped allyl radicals, which have a long life (1060 hr) at room temperature. In the case of PE preirradiated in air Ballantine et al.² have also pointed out that the grafting reaction occurs at 22°C. Furthermore, Shinohara and Tomioka,⁵ and Matsuda et al.⁶ have studied grafting of several monomers by trapped radicals. Ueda⁷ has reported that PE preirradiated in air, exposed to air at room temperature for a day after irradiation, is still able to induce graft copolymerization of vinyl chloride by trapped radicals.

Ohnishi et al.⁸ have followed the behavior of radicals when PE irradiated *in vacuo* is exposed to air. It was suggested that the postoxidation proceeds mainly through allyl radical, but alkyl radical is almost inert. The

* Present address: Chiba Laboratory, Nissan Chemical Industries, Co., Ltd., 11 Goi-Minamikaigan, Ichihara, Chiba, Japan.

peroxy radical, formed immediately after the introduction of air from part of the allyl radical, decays quickly (20 min) to form oxidized products such as peroxide, hydroperoxide, or carbonyl products. The other part of the allyl radical, however, decays slowly and eventually forms oxygenated products (after 130 hr). Matsuda et al.,⁹ Hayakawa and Kawase,¹⁰ and Dobó and Hedvig¹¹ have reported that peroxy radical preirradiated in air is able to initiate grafting in the case of polypropylene-styrene, polypropylene-vinyl chloride, and polytetrafluoroethylene-styrene graft copolymerizations, respectively.

However, it is still not clear what kind of radical (trapped nonoxidized radical or trapped peroxy radical) initiates the low-temperature grafting on polyethylene preirradiated in air. The objective of this work was to learn which radical initiates the grafting reaction of butadiene on polyethylene preirradiated in air by comparing it with the case of preirradiation *in vacuo*.

EXPERIMENTAL PROCEDURE

Materials

The following kinds of PE were used: (a) high-density PE films (PEH; density 0.947 g/cm³, thickness 0.05, 0.1, and 0.5 mm), (b) low-density PE films (PEL; density 0.916 g/cm³, thickness 0.1 and 0.5 mm), and (c) several Marlex-type PE (density 0.957, 0.949, and 0.940 g/cm³, thickness 0.5 mm). Of these films the 0.5 mm films were prepared by hot-pressing in the laboratory, and the others were supplied as commercial films. Their properties are summarized in Table I. The films were soaked in cyclohexanone for 6 hr at 60°C, for 24 hr at room temperature, and in boiling methanol for 2 hr and then were dried *in vacuo* at 50°C for 24 hr. The butadiene monomer (99.5% purity) supplied from the cylinder was

TABLE I
Properties of Polyethylenes Used

Polymer and process	Thick., mm	Molding	Density	Melt index	Cryst. x-ray, %
PEL, high-pressure:	0.5	Press*	0.916	7.0	64
	0.1	Inflation	0.918	7.0	—
	0.5	Press*	0.947	3.5	81
PEH, Ziegler:	0.1	Press and inflat.	0.947	3.5	—
			0.948	—	—
	0.05	Inflat.	0.951	—	—
Sholex, Phillips:	0.5	Press*	0.957	5.0	88
	5065	Press*	0.949	6.5	83
	4002	Press*	0.940	0.2	78
Ethylene-propylene copolymer	Lump		0.87	—	0

* Pressed at 180°C for 5 min and rapidly cooled by cold water.

purified by being washed through 20% NaOH solution and dried through calcium chloride tubes.

Grafting Technique

PE films in ampule were irradiated by gamma rays from a ^{60}Co source. In the case of preirradiation in air an open ampule with a tube containing calcium chloride was used. After irradiation it was degassed for 10 min at -78°C *in vacuo* (10^{-2} mm Hg); this was followed by introducing monomer from a butadiene gas line and sealing after degassing at -78°C *in vacuo*. In the case of preirradiation *in vacuo* PE films were sealed in a vacuum ampule (10^{-2} mm Hg) with a breakable joint. After irradiation the ampule was joined to a butadiene gas line and degassed. When the joint had been broken by a magnet, butadiene gas was introduced from the cylinder in the ampule at -78°C and sealed in. Various irradiation temperatures and irradiation dose rates were employed, from -78 to 50°C and from 1.05×10^4 to 1.4×10^5 rad/hr, respectively. The polymerization temperature and time were 15 to 50°C and 2 to 24 hr, respectively. After completion of the polymerization the PE films were soaked in cyclohexanone at 50°C for 6 hr and at room temperature for a day. Then the films were soaked in hot methanol for 2 hr, after which they were dried *in vacuo* at 50°C . The overall per cent grafting of the film was obtained from the equation $G = 100 \times (W_f - W_i)/W_i$, where W_i and W_f are the initial and final weights of the films, respectively. The crystallinity of the PE films (0.5 mm thick) was determined from x-ray diffraction by means of Matthews' method.¹²

RESULTS AND DISCUSSION

Effect of Polymerization Temperature and Time on Per Cent Grafting

As shown in Figure 1, the grafting of butadiene onto PEH preirradiated in air takes place even at room temperature. The grafting rate is high in the early stages but gradually saturates for a longer polymerization time. These results are similar to those in the case of preirradiation *in vacuo*, as shown in Figure 2. So it is conceivable that both the graftings of butadiene onto PEH preirradiated in air and *in vacuo*, are of the trapped free-radical type.

From the initial slope of the graft conversion curve the initial rate is obtained. The grafting rates at various temperatures are shown in Figure 3. The overall apparent activation energy is about 9.7 kcal/mol for PEH. Little fundamental difference between preirradiation in air and *in vacuo* was observed.

In grafting onto PEL similar results are observed, and the overall apparent activation energy is about 8.4 kcal/mol. However, the time for saturation and the saturation value of the per cent grafting is small compared with the case of PEH (Figs. 4 and 5).

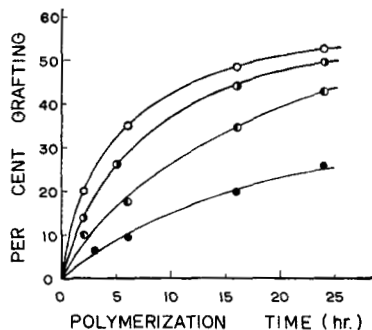


Fig. 1. Per cent grafting versus time for butadiene grafting onto PEH (0.5 mm) preirradiated in air at 15°C at 1.4×10^6 rad/hr for 16 hr, at various temperatures (°C): (●) 15; (◐) 30; (◑) 40; (○) 50.

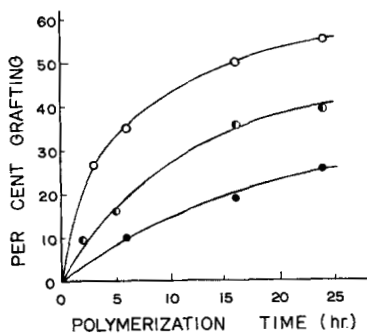


Fig. 2. Per cent grafting versus time for butadiene grafting onto PEH (0.5 mm) preirradiated *in vacuo* at 15°C at 1.4×10^6 rad/hr for 16 hr, at various temperatures (°C): (●) 15; (◐) 30; (○) 50.

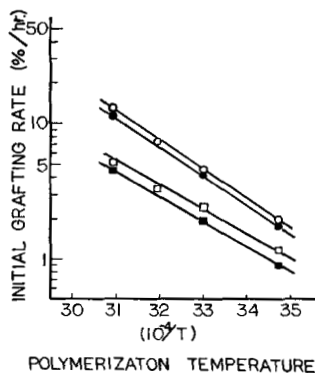


Fig. 3. Initial grafting rate of butadiene, at various temperatures, onto PE (0.5 mm) preirradiated at 15°C at 1.4×10^6 rad/hr for 16 hr: (○) PEH preirradiated in air; (●) PEH preirradiated *in vacuo*; (◻) PEL preirradiated in air; (■) PEL preirradiated *in vacuo*.

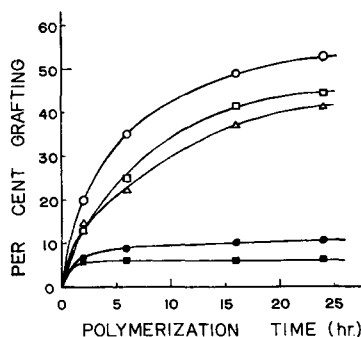


Fig. 4. Per cent grafting versus time for butadiene grafting at 50°C onto various PE films preirradiated in air at 15°C at 1.4×10^5 rad/hr for 16 hr: (○) PEH, 0.5 mm; (□) PEH, 0.1 mm; (△) PEH, 0.05 mm; (●) PEL, 0.5 mm; (■) PEL, 0.1 mm.

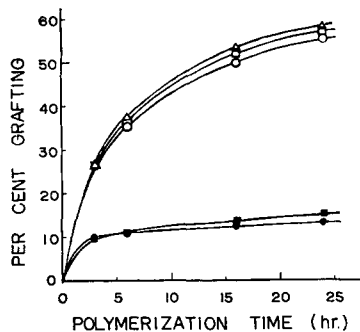


Fig. 5. Per cent grafting versus time for butadiene grafting at 50°C onto various PE films preirradiated *in vacuo* at 15°C at 1.4×10^5 rad/hr for 16 hr: (○) PEH, 0.5 mm; (□) PEH, 0.1 mm; (△) PEH, 0.05 mm; (●) PEL, 0.5 mm; (■) PEL, 0.1 mm.

Effect of Film Thickness on Grafting

In the case of preirradiation in air at 15°C the per cent grafting decreases with decreasing film thickness, as shown in Figure 4. In the case of preirradiation *in vacuo*, however, little difference in per cent grafting between films of different thicknesses is observed, as shown in Figure 5. This means that the grafting is homogeneous throughout the film in the case of preirradiation *in vacuo*, and it suggests that the superficial oxidized (nongrafted) layer will affect the per cent grafting more effectively in thinner films than in thicker in the case of preirradiation in air.

Effect of Irradiation Temperature on Per Cent Grafting

The per cent grafting decreases with increasing irradiation temperature in the range of -19 to 50°C in both preirradiation in air and *in vacuo*, as shown in Figures 6 and 7. The tendency is more remarkable in air than *in vacuo*. This may be due to the decrease in concentration of graft-active radicals (allyl radical) with increasing irradiation temperature, because a recombination of the radicals in both cases and an additional effect of O₂ on

the radical in the case of preirradiation in air are involved. In the latter case the peroxy radical, produced by the combination of some graft-active radicals and diffused oxygen, decays quickly (20 min), as pointed out by Ohnishi et al.⁸

On the other hand, the per cent grafting is lower at -78°C irradiation than at -19°C irradiation. To clarify the result, however, another experiment is required and it will be reported in another paper.

Effect of Preirradiation Dose on Per Cent Grafting

If the grafting proceeds homogeneously throughout the film, the per cent grafting will be proportional to the square root of the concentration of graft-active radical, according to the kinetic theory of free-radical poly-

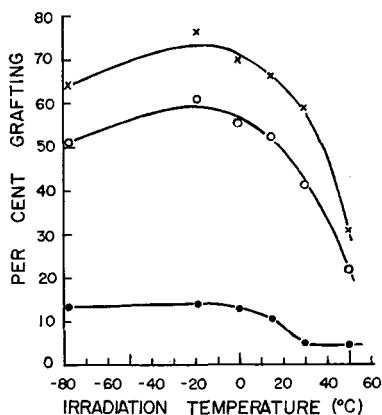


Fig. 6. Per cent grafting of butadiene onto various PE films, at 50°C for 24 hr of polymerization, versus irradiation temperature in air at 1.4×10^5 rad/hr for 16 hr: (X) Sholex 6050, 0.5 mm; (O) PEH, 0.5 mm.; (●) PEL, 0.5 mm.

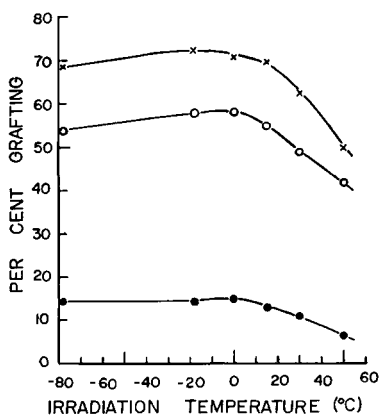


Fig. 7. Per cent grafting of butadiene onto various PE films, at 50°C for 24 hr of polymerization, versus irradiation temperature *in vacuo* at 1.4×10^5 rad/hr for 16 hr; (X) Sholex 6050, 0.5 mm; (O) PEH, 0.5 mm.; (●) PEL, 0.5 mm.

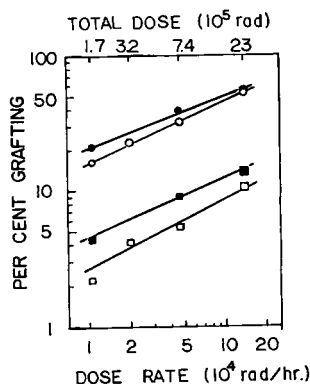


Fig. 8. Per cent grafting of butadiene onto PE (0.5 mm), at 50°C for 24 hr of polymerization, versus irradiation dose rate (or total dose) at 15°C for 16 hr: (O) PEH irradiated in air; (●) PEH irradiated *in vacuo*; (□) PEL irradiated in air; (■) PEL irradiated *in vacuo*.

merization. As shown in Figure 8, the per cent grafting G is represented by the equation

$$\log G = \alpha \log I + \log k$$

$$G = kI^\alpha$$

where I is the dose rate (I is proportional to the total dose in this case, the irradiation time being fixed at 16 hr). The value of α is 0.45 for PEH and 0.51 for PEL preirradiated in air and 0.40 for PEH and 0.45 for PEL preirradiated *in vacuo*. These results almost agree with the kinetic theory, if the concentration of graft-active radical is proportional to the total dose.

Effect of Trunk Polyethylene on Per Cent Grafting

The per cent grafting of butadiene at low-temperature grafting on preirradiated PE is proportional to the density of trunk PE preirradiated in

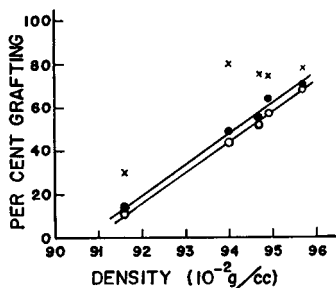


Fig. 9. Per cent grafting of butadiene and styrene onto PE (0.5 mm) of various densities: (O) preirradiated in air at 15°C at 1.4×10^5 rad/hr for 16 hr., polymerized at 50°C for 24 hr.; (●) preirradiated *in vacuo* at 15°C at 1.4×10^5 rad/hr for 16 hr., polymerized at 50°C for 24 hr.; (X) preirradiated in air at 0°C at 1.4×10^5 rad/hr for 4 hr., polymerized at 50°C for 24 hr in styrene.

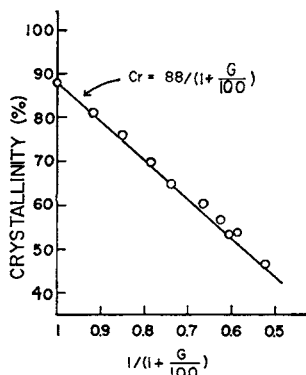


Fig. 10. Overall crystallinity of PE (Sholex 6050) and butadiene graft copolymer.

air and *in vacuo*, as shown in Figure 9. The per cent grafting of 0.957-density PE reaches 7 times that of 0.916-density PE. In addition, it was not possible to graft butadiene onto amorphous ethylene-propylene copolymer (EPR; $d = 0.87$) under the same experimental conditions. From these results it is clear that the crystallinity of trunk polymer is one of the most important factors in the grafting of butadiene by preirradiation technique.

However, Kashiwabara and Shinohara¹³ have found that the ratio of concentrations of trapped radicals in irradiated high-density PE and low-density PE is 5:3, and this value is nearly equal to the ratio of their crystallinities (90:55). If the concentration of trapped radicals, $[R\cdot]$, is equal to the ratio of crystallinity of each PE (88:64), the ratio of per cent grafting of butadiene (7:1) on each PE is not proportional to the square root of $[R\cdot]$. From this result it is supposed that the effect of crystallinity of PE on per cent grafting is due not only to the concentration of trapped radicals but also to other factors, such as the gel effect. For instance, in the case of styrene grafting on preirradiated PE such a proportionality of density as shown by butadiene was not found (Fig. 9).

The overall crystallinity calculated from the x-ray diffraction curve decreases with increasing per cent grafting, as shown in Figure 10. However, this means, not a destruction of the crystallite of PE in the grafting reaction, but a dilution of the crystallinity by the grafting of amorphous polybutadiene.¹⁴

Graft-Active Radicals

If the graft-active radicals decay homogeneously throughout the film, the decreasing curve of per cent grafting versus storage time must be the same for films of different thicknesses. PEH films preirradiated in air at 15°C were stored in air at 50°C. During storage in air a tube containing calcium chloride had been attached to the ampule. It is shown in Figure 11 that per cent grafting decreases more rapidly in thin films than in thick ones. Similar results are observed at 30°C storage in air, a little at 15°C

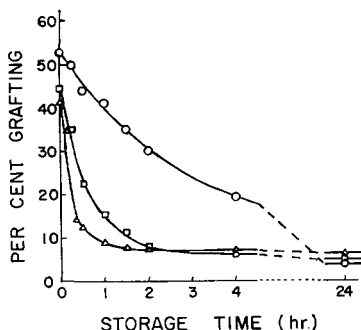


Fig. 11. Decay curves of per cent grafting of butadiene, polymerized at 50°C for 24 hr, onto PEH films of various thicknesses preirradiated in air at 15°C at 1.4×10^5 rad/hr for 16 hr with storage time at 50°C in air: (O) 0.5 mm; (□) 0.1 mm; (Δ) 0.05 mm.

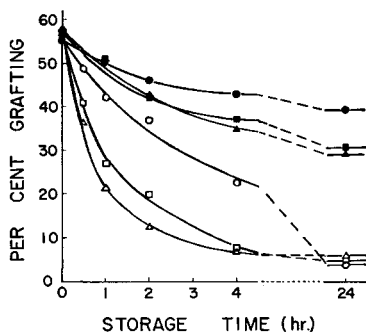


Fig. 12. Decay curves of per cent grafting of butadiene polymerized at 50°C for 24 hr onto PEH films preirradiated *in vacuo* at 15°C at 1.4×10^5 rad/hr for 16 hr with storage time at 50°C. Thickness (mm) and type of storage: (Δ) 0.5, in air; (□) 0.1, in air; (▲) 0.05, in air; (●) 0.5, *in vacuo*; (■) 0.1, *in vacuo*; (▲) 0.05, *in vacuo*.

storage, but none at 0°C storage. This indicates that the graft-active radicals decay from the surface of the film at storage in air above 15°C when PE is irradiated at 15°C in air.

On the other hand, when films are preirradiated *in vacuo* at 15°C and stored in air and *in vacuo* at 50°C, the difference of decreasing curve of each film is much smaller in vacuum storage than in air storage. Moreover, the decrease of per cent grafting even after 24 hr of storage *in vacuo* is smaller than that of storage in air, as shown in Figure 12. When films are stored in air at 50°C, there is little difference in the decreasing behavior of per cent grafting between preirradiation in air and that *in vacuo*.

From these results it is clear that the graft-active radical is inactivated predominantly by oxygen diffused from the surface of the film and that the presence of oxygen during irradiation in air has little effect on the grafting reaction, especially for thick films.

When films of different densities preirradiated *in vacuo* at 15°C are stored in air at 50°C, the relative grafting (G_t/G_0) decreases more rapidly in low-

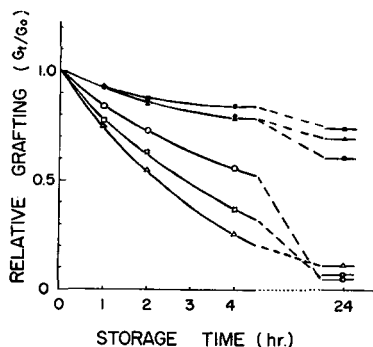


Fig. 13. Decay curves of relative grafting (G_t/G_0) of butadiene polymerized at 50°C for 24 hr onto PE films (0.5 mm) preirradiated *in vacuo* at 15°C at 1.4×10^6 rad/hr for 16 hr versus storage time at 50°C. Density and type of storage: (○) 0.957 in air; (□) 0.949 in air; (△) 0.940, in air; (●) 0.957 *in vacuo*; (■) 0.949 *in vacuo*; (▲) 0.940 *in vacuo*.

density film than in high-density film (G_0 and G_t are per cent grafting at storage time 0 and t , respectively). However, when films are stored *in vacuo* at 50°C, the decreasing curve of each film differs little, and the decreasing of relative grafting is smaller in the case of storage *in vacuo* than of storage in air, as shown in Figure 13. These results are illustrated by the fact that oxygen diffuses more easily in low-density PE than in high-density PE.¹⁵ Similar results are observed in the case of preirradiation in air at 15°C and storage in air at 50°C.

Therefore, it is considered that low-temperature grafting of butadiene onto PE preirradiated in air is initiated by nonoxidized radical trapped in PE.

Region of Grafting Reaction in Polyethylene

As shown in Figure 14, the per cent grafting of butadiene onto high-density PE preirradiated in air at 15°C scarcely decreases after 24 hr of

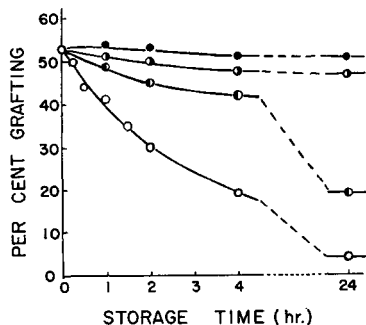


Fig. 14. Decay curves of per cent grafting of butadiene, polymerized at 50°C for 24 hr, onto PEH film (0.5 mm) preirradiated in air at 15°C at 1.4×10^6 rad/hr for 16 hr, versus storage, in air, time. Temperature (°C): (●) 0; (◐) 15; (◑) 30; (○) 50.

storage in air below 15°C. According to this consideration, this means that the graft-active radical is scarcely oxygenated below 15°C after 24 hr of storage in air. In addition, the per cent grafting is proportional to the density of trunk PE, and in amorphous EPR the grafting reaction does not occur, as mentioned above. From these results it is considered that the graft-active radical is trapped by the crystalline part of PE, and oxygen diffuses with difficulty into the region in which the radical is trapped. This consideration is supported by the ESR result reported by Ohnishi et al.⁸ as follows:

"Thus the ESR results might suggest that oxidation of $FR_{V_{11}}$ (allyl radical) takes place in stages. Immediately after introduction of air, part of the $FR_{V_{11}}$ reacted to form the peroxide radical ($FR_{V_{11}}O_2\cdot$), which decayed quickly to one half in 20 min. In the second stage (about 3–130 hr), some oxygenated radicals of other type appeared. In the third stage (>130 hr), $FR_{V_{11}}$ decayed almost entirely to form oxidation products, and polyenyl radicals of longer conjugations remained."

It is considered then that the part of allyl radical which decays in the first stage will be produced in the amorphous region. Another allyl radical, which decays in the third stage, will be produced in the crystalline part of PE, and it is able to initiate the grafting reaction after 24 hr of storage in air below 15°C.

However, the per cent grafting decreases largely above 15°C by storage in air after irradiation in air at 15°C (Fig. 14). Furthermore, it decreases by storage even *in vacuo* at 50°C (Figs. 12 and 13). These results indicate that the graft-active radical is inactivated by oxygen in the case of storage in air, and the radical also disappears by recombination in the case of storage *in vacuo*, even at the temperature under the melting point of PE crystallite, respectively. In the case of preirradiation *in vacuo* it is suggested that the recombination of graft-active radical is increased with increasing irradiation temperature (Fig. 7). In order to combine two allyl radicals, the polymer chain must be mobile, because the radical will not be able to migrate along it.¹⁶ In addition, it is suggested that crystallite (lamella) of PE is not destroyed by the grafting reaction (Fig. 10). This indicates that the grafting does not occur in the inner part of the crystallite (lamella) of PE.

From these considerations it is concluded that the grafting reaction is initiated by the allyl radical, which is trapped in a somewhat mobile region of the crystalline part. This region will be the surface or the defect of PE crystallite (lamella), i.e., the so-called semicrystalline part.¹⁷ In other words, this region will be one of the amorphous regions in which chain mobility is restrained strongly by crystallite.

It is not still clear what role is played by the radicals trapped in the inner part of the crystallite: i.e., whether alkyl radical migrates from the inner part of crystallite to the region of grafting and is converted to allyl radical.¹⁶ To clarify this problem another experiment is required, and it will be reported in another paper.

CONCLUSION

It is concluded that the low-temperature grafting of butadiene onto PE preirradiated in air is initiated predominantly by nonoxidized radical (allyl radical) trapped in PE and that the grafting reaction occurs in the so-called semicrystalline part (surface or defect of PE crystallite).

The authors wish to thank J. Sohma and H. Kashiwabara for their valuable discussions and K. Yoshikawa for his assistance with some of experiments.

References

1. A. Chapiro, *Radiation Chemistry of Polymeric Systems*, Interscience, New York 1962.
2. D. S. Ballantine, A. Glines, G. Adler, and D. J. Metz, *J. Polymer Sci.*, **34**, 419 (1959).
3. N. Tamura, H. Tachibana, T. Takamatsu, and K. Shinohara, *Rept. Progr. Polymer Phys. Japan*, **6**, 269 (1963).
4. N. Tamura, H. Tachibana, T. Takamatsu, and K. Shinohara, *Rept. Progr. Polymer Phys. Japan*, **6**, 273 (1963).
5. Y. Shinohara and K. Tomioka, *J. Polymer Sci.*, **44**, 195 (1960).
6. T. Matsuda, Y. Sakai, and H. Yamakita, *Kobunshi Kagaku*, **19**, 313 (1962).
7. K. Ueda, *Kobunshi Kagaku*, **23**, 222 (1966).
8. S. Ohnishi, S. Sugimoto, and I. Nitta, *J. Polymer Sci. A*, **1**, 605 (1963).
9. T. Matsuda, B. Eda, and K. Nunome, *Proc. 5th Conf. Radioisotopes, Japan*, 4-109 (1963).
10. K. Hayakawa and K. Kawase, *J. Polymer Sci. A-1*, **4**, 439 (1967).
11. J. Dobó and P. Hedvig, in *Macromolecular Chemistry, Prague 1965 (J. Polymer Sci. C*, **16**), O. Wichterle and B. Sedláček, Chairmen, Interscience, New York, 1967, p. 2577.
12. J. L. Matthews, H. S. Peiser, and R. B. Richards, *Acta Cryst.*, **2**, 85 (1949).
13. H. Kashiwabara and K. Shinohara, *J. Phys. Soc. Japan*, **15**, 1129 (1960).
14. A. Furuhashi and M. Kadonaga, *J. Appl. Polymer Sci.*, **10**, 127 (1966).
15. A. S. Michaels and R. B. Parker, Jr., *J. Polymer Sci.*, **41**, 53 (1959).
16. A. Charlesby, D. Libby, and M. G. Ormerod, *Proc. Roy. Soc. (London)*, **A262**, 207 (1961).
17. H. Kashiwabara, *Rept. Progr. Phys. Japan*, **6**, 257 (1963).

Received February 20, 1968

Revised April 10, 1968