

Radiation-Induced Graft Copolymerization of Butadiene to Polyethylene and Polypropylene

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Synopsis

Polyethylene and polypropylene films were irradiated by γ -irradiation from a Co^{60} source in butadiene gas flow and in liquid butadiene. Irradiating in the butadiene gas flow is particularly convenient because the gas state monomer is available directly and little homopolymer is produced. In this case, there is a retardative effect on the grafting near the surface of the film and the grafting rate shows the maximum values at 50–60°C. for high-density PE (PEH) and PP. Irradiating in the liquid butadiene decreases the retardative effect near the surface. The effect of dose rate I on the grafting rate R_p is represented by $R_p \propto I^{1/4}$ in this case. The grafting rate is always higher in PEH than in low-density PE (PEL). Results of x-ray diffractometry and electron microscopy indicate that the grafting reaction occurs predominantly near the surface of the crystallite (lamella) of PE and the grafting rate is not affected by the overall crystallinity of the trunk polymer but by the configurational structure, such as the degree of branching or side-chain length.

INTRODUCTION

During the past few years a number of experiments on radiation-induced graft copolymerization have been done.¹ There are few reports, however, on grafting of monomers which have conjugated double bonds onto polyolefins. Polyolefin-butadiene graft copolymers have been obtained by γ -irradiation of polyolefins in a butadiene gas flow. This technique is particularly convenient because the monomer is available directly in the gas state and little homopolymer is produced.²

In the present work, this technique was compared with the simultaneous irradiation grafting technique in liquid butadiene to examine the effect of several factors on the grafting, such as irradiation time, dose rate, temperature, film thickness, and crystallinity of the trunk polymer. The changes of the microstructural characteristics of polyethylene during the grafting reaction were followed by the use of x-ray diffractometry and electron microscopy.

EXPERIMENTAL PROCEDURE

Materials

As trunk polymers for graft copolymerization, the following polymers were used; (a) high-density polyethylene films (PEH; density, 0.955 g./cc.; thickness, 0.02, 0.05, 0.1, 0.35, 0.5 mm.), (b) low-density polyethylene films (PEL; density, 0.921 g./cc.; thickness, 0.05, 0.5 mm.), and (c) polypropylene films, (PP; thickness, 0.03, 0.5 mm.). Of these films, the 0.5-mm. thick films were molded by pressing in our laboratory and the others were commercial films. These films were soaked in cyclohexanone for 6 hr. at 60°C. and then for 24 hr. at room temperature, followed by drying *in vacuo* at 50°C for 24 hr. The butadiene monomer gas (99.5% purity) from the cylinder was purified by washing through 20% NaOH solution and dried through calcium chloride tubes.

Grafting Technique

Polymer films were irradiated by γ -rays from a 4000-curie Co^{60} source under butadiene gas flow through the ampule in which the air had been displaced by the gas. A schematic diagram of the apparatus for irradiation in gas flow is shown in Figure 1. The flow rate of butadiene was 0.5 l./min., and the pressure was slightly higher than ambient.

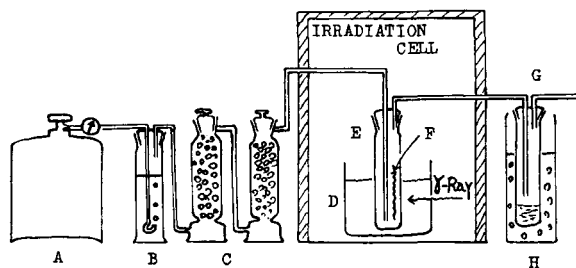


Fig. 1. Apparatus for the grafting in butadiene gas: (A) butadiene; (B) 20% NaOH solution; (C) CaCl_2 tube; (D) thermostat, (E) reaction tube, (F) sample, (G) trap, (H) Dry Ice-methanol vessel.

For irradiation in liquid butadiene, the films were sealed in the ampule after being degassed repeatedly at -78°C . *in vacuo*. The pressure of the liquid butadiene in the sealed ampules was equal to the vapor pressure of butadiene at the reaction temperature (for instance, 5.2 atm. at 50°C .). Various irradiation dose rates, temperatures, and times were employed, extending from 1.2×10^4 to 2.3×10^5 rad/hr., from 0 to 80°C ., and from 2 to 46 hr., respectively. Immediately after completion of the irradiation, the films were taken from the ampule and degassed at 50°C . *in vacuo*. To remove occluded butadiene homopolymer, the films were soaked in cyclohexanone at 55°C . for 6 hr. and then at room temperature for 24 hr., followed by drying *in vacuo* at 50°C . The overall per cent grafting of the

film G was obtained from the equation $G = 100 \times (W_f - W_i)/W_i$, where W_i and W_f are initial and final weights of the film, respectively.

Observation Technique

The distribution of the graft concentration in the graft copolymer film was observed by the interferometric method which was developed by Matsuo et al.³ The crystallinities of the polyethylene films (0.5 mm. thick) were determined from x-ray diffraction by means of Matthews' method.⁴ To observe structural details in PEH and PEH-butadiene graft copolymer, a replication procedure for electron microscopy was applied. The structures of the grafted polybutadiene were estimated by infrared absorption spectra.

RESULTS AND DISCUSSION

Effect of Irradiation Time on the Per Cent Grafting

As shown in Figure 2, when the films are irradiated in butadiene gas, the per cent grafting is directly proportional to the irradiation time except in the case of thin films. This observation was noticed within the range of irradiation temperatures and dose rates employed in this experiment.

On the other hand, when the films were irradiated in liquid butadiene, the per cent grafting levels off slightly for a longer irradiation time,

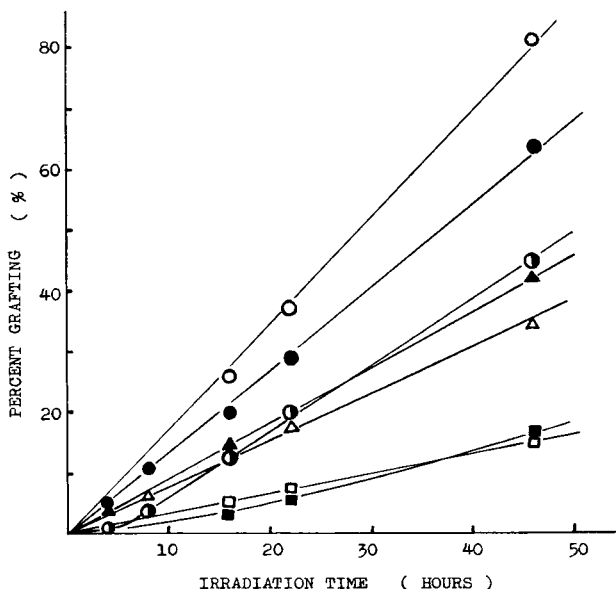


Fig. 2. Grafting of butadiene to various polyolefin films under irradiation in the butadiene gas flow at 50°C., 2.3×10^6 rad/hr.: (○) PEH, 0.5 mm.; (●) PEH, 0.05 mm.; (◐) PEH, 0.02 mm.; (◻) PEL, 0.5 mm.; (◼) PEL, 0.05 mm.; (△) PP, 0.5 mm.; (▲) PP, 0.03 mm.

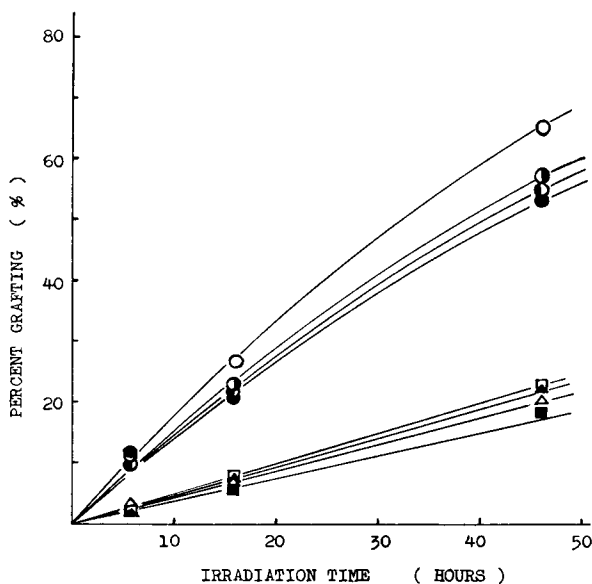


Fig. 3. Grafting of butadiene to various polyolefin films under irradiation in liquid butadiene at 50°C., 2.3×10^6 rad/hr.: (○) PEH, 0.5 mm.; (●) PEH, 0.1 mm.; (●) PEH, 0.05 mm.; (◐) PEH, 0.02 mm.; (□) PEL, 0.5 mm.; (■) PEL, 0.05 mm.; (△) PP, 0.5 mm.; (▲) PP, 0.03 mm.

resulting in an amount of occluded butadiene homopolymer, as shown in Figure 3 and Table I. These observations can be explained by considering that, in addition to polymer radicals and growing graft copolymer radicals, monomer radicals and other radicals are created in the sealed ampule increasingly with irradiation time, and eventually they induce homopolymerization and termination reaction.

TABLE I
Effect of Irradiation Technique on the Quantity of Butadiene Homopolymer Extracted by Cyclohexanone from 0.05 mm. Film after Irradiation at 50°C., 2.3×10^6 rad/hr., for 22 hr.

Irradiation	Grafting, %		Homopolymer (A) - (B), %
	A Before extraction	B After extraction	
In butadiene gas	30.2	29.0	1.2
In liquid butadiene	38.8	27.5	11.3

Retardative Effect Near the Surface

When the grafting reaction occurs homogeneously throughout the film, the film thickness does not affect the overall grafting rate. As shown in Figures 1 and 2, it was experimentally found for the PE-butadiene grafting

reaction, especially when PE was irradiated in the butadiene gas flow, that the grafting rate increased with increasing film thickness. On the other hand, for the PP-butadiene reaction the rate was higher for the 0.03-mm. film than for the 0.5-mm. thick film.

Distributions of the graft concentration in the graft copolymer films as determined by interferometry are shown in Figures 4 and 5. Figures

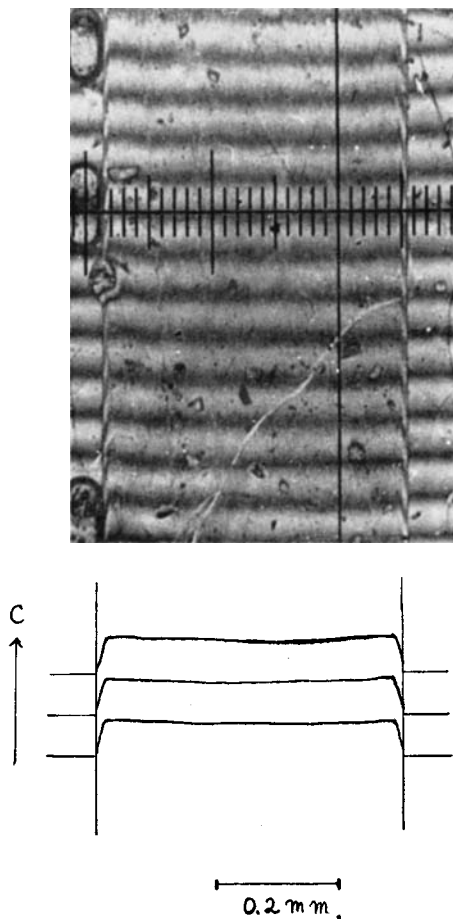


Fig. 4. Distribution of the graft concentration in PEH-butadiene graft copolymer film (0.5 mm.), irradiated in the butadiene gas at 50°C., 8.4×10^6 rad/hr., for 46 hr.; $G = 59.3\%$.

4 and 5 clearly show that in PP film, the graft concentration is lower near the center of the film, as grafting is controlled by diffusion of monomer, and a retardative effect on grafting appears near the film surface. In PE film, the graft concentration is homogeneous throughout the film, but there is a retardative effect on grafting near the film surface. The depth from the surface at which this effect is operative, is approximately 10μ .

An anomalous phenomenon near the surface had been reported in detail by Matsuo et al.³ in the case of PE-styrene graft copolymerization in methanol solution. This retardative effect can be interpreted by considering that the grafting rate constant becomes low when monomer concentration in the film increases, as Matsuo had pointed out, and consequently

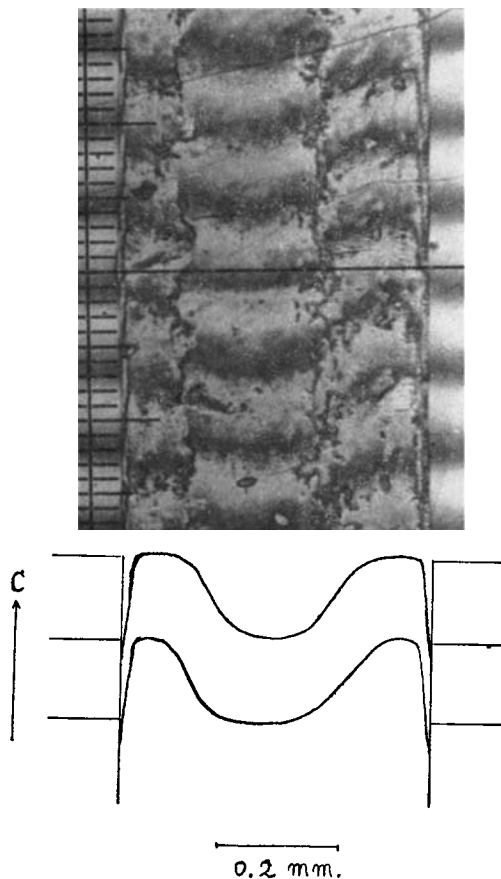


Fig. 5. Distribution of the graft concentration in PP-butadiene graft copolymer film (0.5 mm.), irradiated in the butadiene gas at 50°C., 8.4×10^6 rad/hr., for 46 hr.; $G = 26.7\%$.

the effect extends to the interior with decreasing dose rate and increasing irradiation temperature.

The decrease of the effect in the liquid-phase grafting reaction may be attributed to the fact that the monomer concentration is almost homogeneous throughout the material owing to a higher pressure of the reaction system and/or that the grafting rate constant is affected by the high pressure of the system.⁵

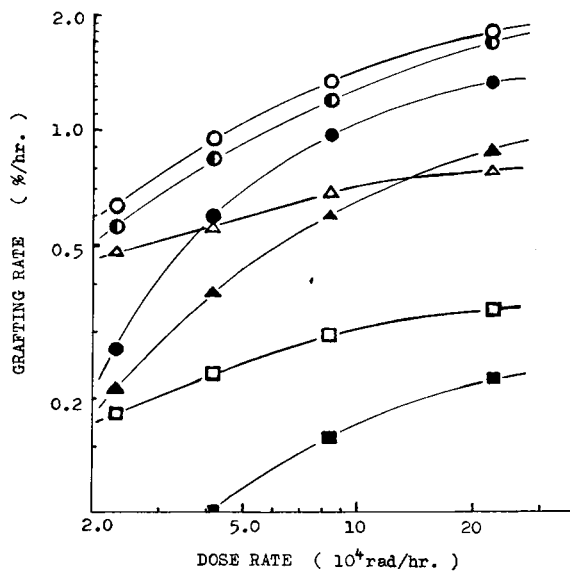


Fig. 6. Effect of dose rate on the grafting rate of butadiene to various polyolefin films under irradiation in the butadiene gas flow at 50°C.: (○) PEH, 0.5 mm.; (●) PEH, 0.1 mm.; (●) PEH, 0.05 mm.; (□) PEL, 0.5 mm.; (■) PEL, 0.05 mm.; (△) PP, 0.5 mm.; (▲) PP, 0.03 mm.

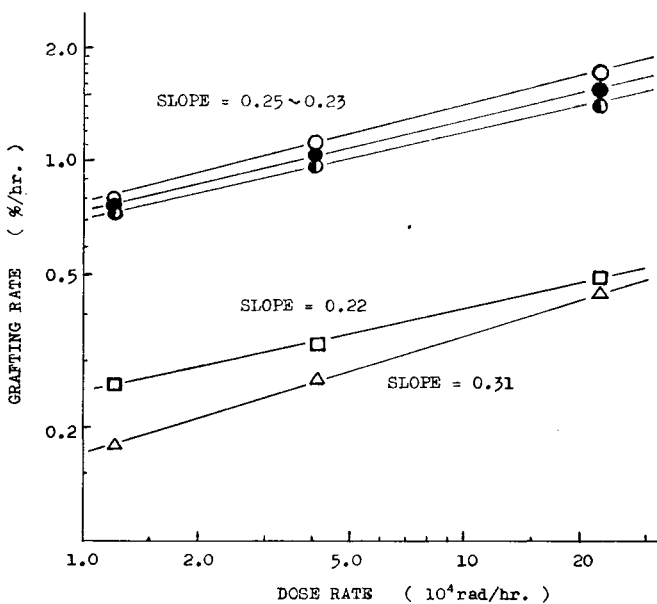


Fig. 7. Effect of dose rate on the grafting rate of butadiene to various polyolefin films under irradiation in the liquid butadiene at 50°C.: (○) PEH, 0.5 mm.; (●) PEH, 0.1 mm.; (●) PEH, 0.05 mm.; (□) PEL, 0.5 mm.; (△) PP, 0.5 mm.

Effect of Irradiation Dose Rate on the Grafting Rate

Results of the dose rate study are shown in Figures 6 and 7. In the case of PE-butadiene graft copolymerization in liquid butadiene, where the graft copolymerization was almost a volumetric reaction, a 0.25-order dependence of the grafting rate on dose rate was found. For PP-butadiene graft copolymerization in liquid butadiene, a 0.31-order dependence of the overall grafting rate on dose rate was found experimentally.

In the case of graft copolymerization in the butadiene gas flow, the dependence by the overall grafting rate on dose rate is complicated. In this case, the overall grafting rate decreases with decreasing dose rate. The thinner the film, the more the rate decreases for the same polymer. This phenomenon is illustrated by the fact that the retardative effect near the surface increases with increasing dose rate,³ and the thinner the film is, the more the overall grafting rate is affected.

Effect of Irradiation Temperature on the Grafting Rate

When the films are irradiated in butadiene gas, the grafting rate increases with increasing irradiation temperature except the case of PEL. The rate shows a maximum value at 50–60°C., as shown in Figure 8. In the case of PEL, the maximum appears at approximately 20°C.

As the cohesion of chain in trunk polymer relaxes, the polymer radicals become mobile and the rate of combination of the radicals increases immediately. The temperature at which the cohesion of the chain relaxes differs, depending on the chemical structure of the polymer,⁶ and consequently the maximum grafting rate for different polymers appears at different temperatures. The maximum grafting rate for PEH, which has

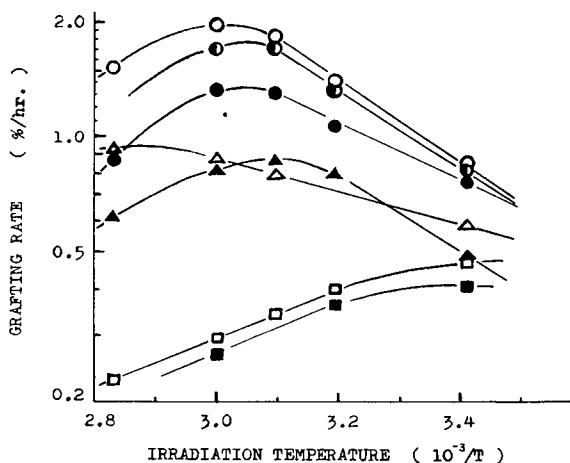


Fig. 8. Effect of irradiation temperature on the grafting rate of butadiene to various polyolefin films under irradiation in the butadiene gas at 2.3×10^6 rad/hr.: (○) PEH, 0.5 mm.; (●) PEH, 0.1 mm.; (●) PEH, 0.05 mm.; (□) PEL, 0.5 mm.; (■) PEL, 0.05 mm.; (△) PP, 0.5 mm.; (▲) PP, 0.03 mm.

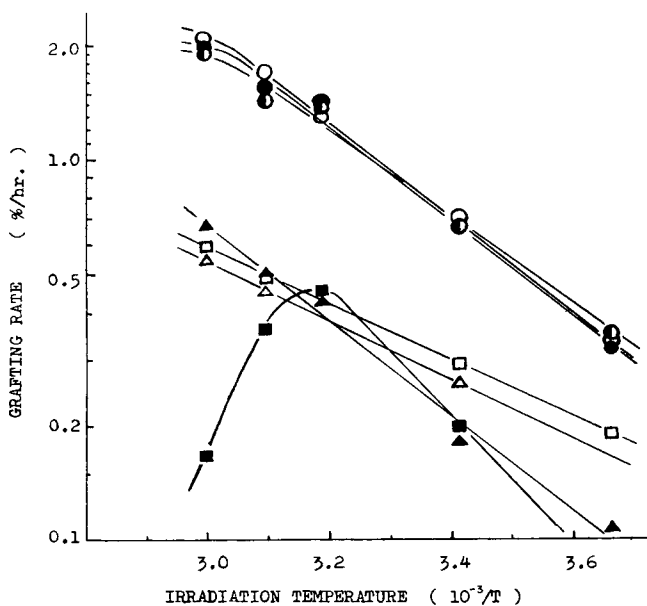


Fig. 9. Effect of irradiation temperature on the grafting rate of butadiene to various polyolefin films under irradiation in the liquid butadiene at 2.3×10^5 rad/hr.: (○) PEH, 0.5 mm.; (◐) PEH, 0.1 mm.; (◑) PEH, 0.05 mm.; (□) PEL, 0.5 mm.; (■) PEL, 0.05 mm.; (△) PP, 0.5 mm.; (▲) PP, 0.03 mm.

a higher softening temperature than PEL, appears at a higher temperature than that for PEL. The difference in grafting rates with varying film thickness is due to the retardative effect near the surface.

As shown in Figure 9, when the films are irradiated in liquid butadiene, the maximum grafting rate appears at higher temperature than in the case of grafting in butadiene gas, especially for PEL. This may be due to the effect of the higher pressure of the system on the grafting rate constant.⁵

Since the grafting rate constant decreases when monomer concentration in the film increases, as mentioned above to explain the retardative effect near the surface, the grafting rate in butadiene gas must be higher than that in liquid butadiene. The results were in agreement with this consideration, as the effect by the higher pressure of the system and the retardative effect near the surface are negligible.

Effect of Structure of Trunk Polymer on the Grafting Rate

The grafting rates are different, depending on the kind of polymer. For the same thickness films of PE, the grafting rate is always higher in PEH than in PEL as shown in Figures 6-9. This fact suggests that the grafting reaction occurs in the crystalline part of PE. However, the result is at variance with the grafting behavior of vinyl chloride onto PE.² According to the generally accepted explanation, according to which the

TABLE II
Effect of Kind of Polyethylene on the Grafting of Various Monomers
to Polyethylene under Irradiation in Liquid Monomer at
50°C., 2.1×10^6 rad/hr. (0.5 mm. Thick Film)

	Crystallinity, %	Grafting rate, %/hr.		
		Butadiene	Styrene	MMA
PEH	87.5	1.68	22.1	20.0
PEL	63.7	0.48	8.1	46.5

grafting reaction is considered to occur exclusively in an amorphous part of the trunk polymer,^{1,2} a higher grafting rate would be expected in PEL than in PEH. As shown in Table II, the grafting rate is higher in PEL than in PEH for PE-methyl methacrylate graft copolymerization but is higher in PEH than in PEL for PE-styrene graft copolymerization, as reported by Hoffman et al.⁸

To clarify the problem of whether the grafting reaction occurs in the crystalline parts of PE the crystalline states of PEH 0.5 mm. film were examined by means of x-ray diffraction before and after grafting. In each

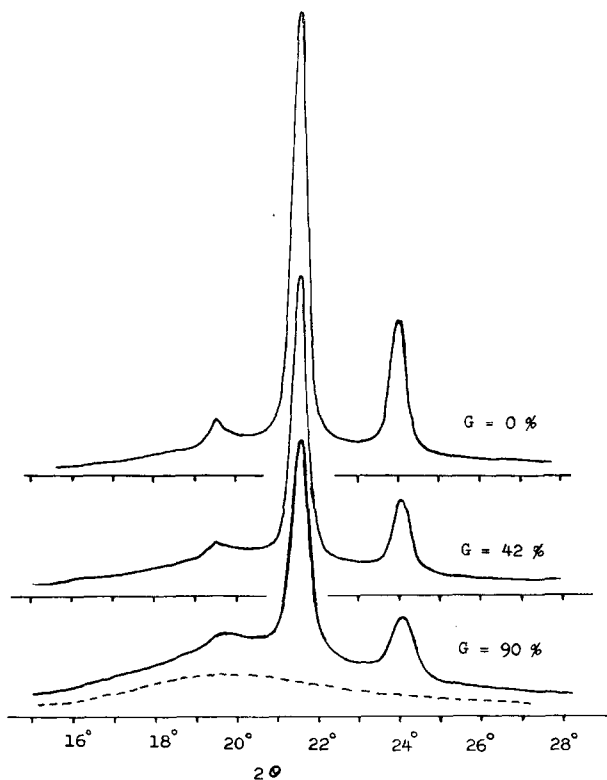


Fig. 10. X-ray diffraction curves of (—) PEH-butadiene graft copolymer and (---) polybutadiene.

diffraction curve, as shown in Figure 10, it was observed that there were three peaks at $2\theta_{110} = 23.65^\circ$, $2\theta_{200} = 21.25^\circ$, and $2\theta_a = 19.20^\circ$. Of these peaks, the third one represents an amorphous part. Moreover there was no variation in the half width of the (110) peak, even after the completion

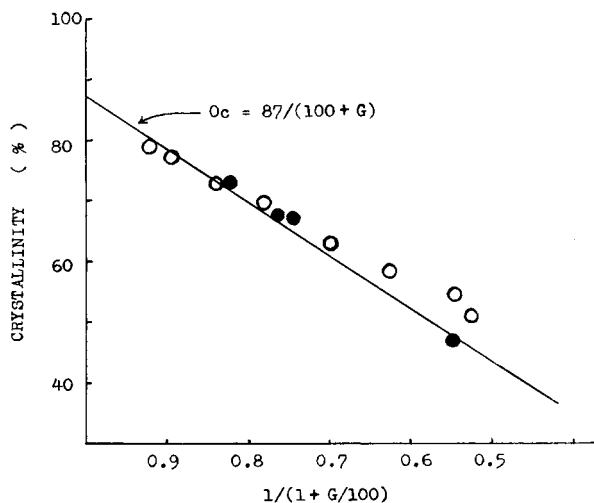


Fig. 11. Over-all crystallinity of PEH-butadiene graft copolymer: (○) irradiation in butadiene gas; (●) irradiation in liquid butadiene.

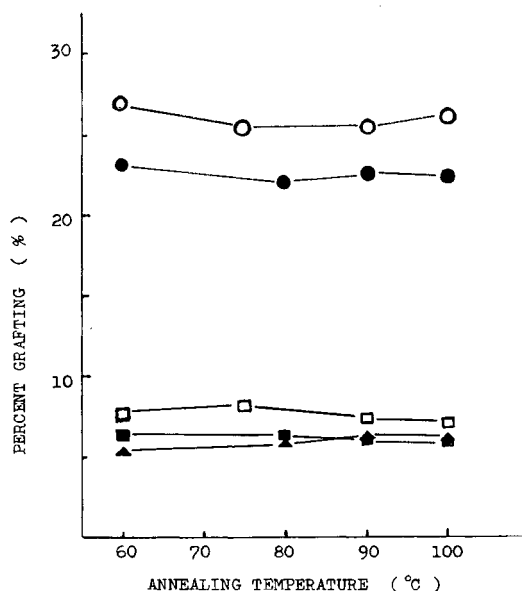


Fig. 12. Effect of annealing temperature for 5 hr. on the grafting of butadiene to various polyolefin films (0.5 mm.) under irradiation in liquid butadiene at 50°C ., 2.1×10^6 rad/hr., for 16 hr.: (○) PEH annealed in air; (●) PEH annealed *in vacuo*; (□) PEL annealed in air; (■) PEL annealed *in vacuo*; (▲) PP annealed *in vacuo*.

of the grafting reaction. These results suggest that the crystal lattice and the crystallite size of PEH are not varied by the grafting reaction.

On the other hand, the overall crystallinity, calculated from the area of the crystalline peaks, decreases with increasing per cent grafting as shown in Figure 11. The diffraction curve of amorphous polybutadiene shows



Fig. 13. Xylene-etched PEH. Ge-shadowed film, two-stage replica. ($\times 4000$)



Fig. 14. Xylene-etched PEH-butadiene graft copolymer. Ge-shadowed film, two-stage replica. ($\times 4000$).

TABLE III
Effect of Crystallinity on the Grafting of Butadiene to PEH 0.35 mm.
Film under Irradiation at 50°C., 2.3×10^6 rad/hr., for 22 hr.

	Irradiation	Crystallinity, %	Grafting, %
Quenched PEH	In butadiene gas	87.0	31.3
Annealed PEH		93.0	29.7
Quenched PEH	In liquid butadiene	87.0	30.7
Annealed PEH		93.0	32.5

a peak at the same angle as the amorphous PE. Assuming that the interference intensity of diffraction of the grafted polybutadiene is equal to that of amorphous PE, the overall crystallinity (O_c) of the PEH-butadiene graft copolymer can be expressed by the equation: $O_c = 87/(100 + G)$, where 87 is the crystallinity of PEH and G is the per cent grafting. The results of the experiment were in accordance with this equation. Therefore, the decrease of the overall crystallinity of PE-butadiene graft copolymer with increasing per cent grafting does not suggest the destruction of the crystallite by grafting but dilution of the crystallinity by grafting of amorphous polybutadiene.

As shown in Table III and Figure 12, the per cent grafting was not affected by changing the relative amorphous volume of trunk polymers by heat treatment.

From the result of the electron microscopic study on the structure of PEH and PEH-butadiene graft copolymer, as shown in Figures 13 and 14, it is evident that after xylene-etching the graft copolymer did not show any spherulitic structure. This result suggests that although the grafting reaction does not destroy crystallites (lamella) of PE, it affects the spherulitic structure of PE.

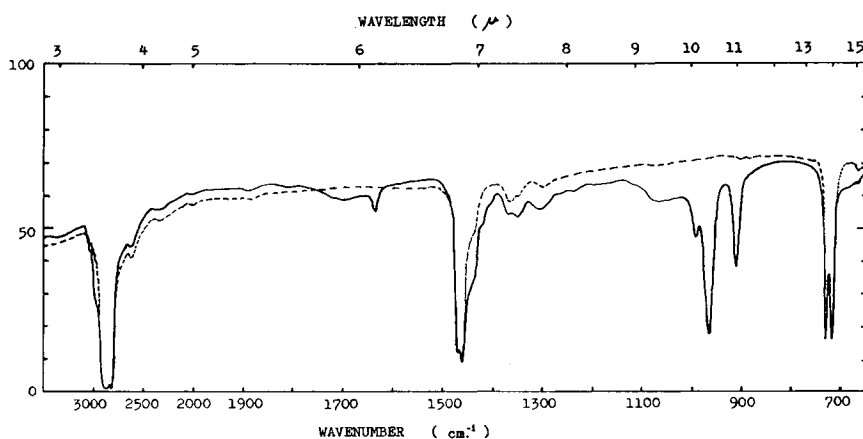


Fig. 15. Infrared absorption spectra: (--) PEH, (—) PEH-butadiene graft copolymer ($G = 28.4\%$).

From these results, it is concluded that (a) the grafting reaction occurs predominantly near the surface of the crystallite (lamella) of PE, (b) the grafting rate is not affected by the overall crystallinity of the trunk polymer but is affected by the degree of branching or side-chain length, and (c) each polymer radical, such as $-\text{CH}_2-\dot{\text{C}}\text{H}-\text{CH}_2-$, $(-\text{CH}=\text{CH}-)_n-\dot{\text{C}}\text{H}-\text{CH}_2-$, $-\text{CH}_2-\dot{\text{C}}(\text{R})-\text{CH}_2-$, $(-\text{CH}=\text{CH}-)_n-\dot{\text{C}}(\text{R})-\text{CH}_2-$, $-\text{CH}(\text{CH}_3)-\text{CH}_2-\dot{\text{C}}(\text{CH}_3)-\text{CH}_2-$, $(-\text{C}(\text{CH}_3)=\text{CH}-)_n-\dot{\text{C}}(\text{CH}_3)-\text{CH}_2-$, ($n=1, 2, 3, \dots$, $\text{R} = \text{CH}_3, \text{C}_2\text{H}_5, \dots$) has a different life, and consequently it affects the grafting rate differently.

These conclusions will be applicable to the grafting of such monomers onto PE as butadiene, isoprene, and styrene which have comparatively lower rates of polymerization.

On the other hand, monomers such as vinyl chloride and methyl methacrylate have higher rates of polymerization. The usual pattern of grafting occurs for these monomers; i.e., the grafting rate is higher for PEL than PEH, because the grafting rate is more influenced by the diffusion rate of the monomer than other factors such as the lives of polymer radicals.

Structure of the Grafted Polybutadiene

The infrared absorption spectra of PEH (0.02 mm. thick) and PEH (0.02 mm.)-butadiene graft copolymer are shown in Figure 15. In the spectrum of the graft copolymer, it was observed that there were four absorption bands at approximately 1640, 995, 968, and 910 cm^{-1} which were not observed in the spectrum of PEH. These bands originate from grafted polybutadiene i.e., the bands at 1640, 995, and 910 cm^{-1} are due to $\text{CH}_2=\text{CH}-$, and the band at 968 cm^{-1} is a *trans* $-\text{CH}=\text{CH}-$ absorption. The band at 740 cm^{-1} which is assigned to *cis* $-\text{CH}=\text{CH}-$ could not be distinguished clearly from the bands of PEH at 730 and 720 cm^{-1} . It was observed, however, that there was a trace of absorption due to *cis* $-\text{CH}=\text{CH}-$ in the spectrum of the graft copolymer.

The spectrum of grafted polybutadiene is similar to that of polybutadiene polymerized in emulsion state by radical catalyst.⁸ Assuming that the grafted polybutadiene does not contain *cis* $-\text{CH}=\text{CH}-$ structure, the double bonds of grafted polybutadiene consist of *trans* $-\text{CH}=\text{CH}-$ (about 78%) and $\text{CH}_2=\text{CH}-$ (about 22%) in all cases.

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Résumé

Des films de polyéthylène et de polypropylène ont été irradiés par des rayons- γ du cobalt-60 dans un flux de butadiène, gazeux et à l'état liquide. L'irradiation dans un flux de butadiène gazeux est particulièrement facile parce que le monomère à l'état gazeux est directement disponible et que peu d'homopolymère est produit. Dans ce cas, il y a un effet retardateur en ce qui concerne le greffage à la surface du film et la vitesse de greffage manifeste un maximum aux valeurs de 50–60°C pour PEH (haute densité) et PP. L'irradiation dans le butadiène liquide décroît cet effet retardateur au niveau de la surface. L'effet de la vitesse de dose (I) sur la vitesse de greffage $R_p \propto I^{1/4}$ dans ce cas. La vitesse de greffage est toujours plus élevée dans le PEH que dans le PEL (faible densité). Au départ des résultats obtenus par diffractométrie aux rayons-X et par microscopie électronique, on a conclu que la réaction de greffage se passe essentiellement au voisinage de la surface des cristallites (lamelles) du PE et que la vitesse de greffage n'est pas affectée par la cristallinité globale du polymère tronc mais la structure configurationnelle telle que le degré de branchement et la longueur des chaînes latérales.

Zusammenfassung

Polyäthylen- und Polypropylenfilme wurden mit Co^{60} - γ -Strahlen in strömendem Butadiengas und in flüssigem Butadien bestrahlt. Die Bestrahlung in strömendem Butadiengas ist besonders gut geeignet, da das gasförmige Monomere direkt reagiert und wenig Homopolymeres erzeugt wird. In diesem Fall tritt ein Verzögerungseffekt bei der Pflropfung in der Nähe der Filmoberfläche auf, und die Pflropfungsgeschwindigkeit zeigt Maximalwerte bei 50–60°C für PEH (hohe Dichte) und PP. Bestrahlung in flüssigem Butadien setzt den Verzögerungseffekt in der Nähe der Oberfläche herab. Der Einfluss der Dosisleistung (I) auf die Pflropfungsgeschwindigkeit (R_p) wird in diesem Fall durch $R_p \propto I^{1/4}$ dargestellt. Die Pflropfungsgeschwindigkeit ist in PEH immer höher als in PEL (niedrige Dichte). Aus den mit dem Röntgendiffraktometer und dem Elektronenmikroskop erhaltenen Ergebnissen kommt man zu dem Schluss, dass die Pflropfreaktion vorwiegend in der Nähe der Kristallitoberfläche (Lamelle) von PE stattfindet und dass die Pflropfgeschwindigkeit nicht durch die Bruttokristallinität des Stammpolymeren, sondern durch die Konfigurationsstruktur, wie Verzweigungsgrad oder Länge der Seitenkette beeinflusst wird.

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