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Radiation-Induced Graft Reaction of Polyethylene with Unsaturated and Carbonyl Compounds as Photo-Oxidative Degradable Groups

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In order to give a photo-oxidative degradable nature to polyethylene, γ -ray-induced graft reaction of unsaturated and carbonyl compounds was studied. The grafting was performed in an atmosphere of these compounds with thin films by the in-source γ -irradiation technique at room temperature. A large amount of 1,3-butadiene or an α , β -unsaturated carbonyl monomer was grafted to polyethylene. Especially, the amount of grafted monomers were increased by co-grafting of the mixture of these monomers. According to the role of unsaturated carbonyl compounds to the graft copolymerization of the mixture with butadiene, these compounds can be divided into two types: one made the increase in only the amount of combined butadiene with the constant ratio of terminal vinyl to *trans*-vinylene unsaturation, but gave little increase in that of a carbonyl compound. The other made the increase in the amount both of combined monomers, and the ratio of terminal vinyl to *trans*-vinylene changed with the molar ratio of the mixture. With the use of the mixture of acetylene and acrolein, acetylene accelerated the increase in the amount of combined acrolein with cross-linking reaction, but gave little increase in that of combined acetylene.

I. INTRODUCTION

Recently, in order to make the disposing of waste plastics easy, several methods, which give a photo-oxidative degradable nature to plastics, such as co-polymerization with an unsaturated ketone¹⁾ and blending a photo-sensitizer with plastics²⁾ have been investigated.

It has been known that unsaturated and carbonyl compounds absorb Ultraviolet light to form radicals. In order to give a photo-oxidative degradable nature to polyethylene, the graft polymerization of unsaturated and carbonyl compounds by the in-source γ -irradiation technique was studied.

II. EXPERIMENTAL

Samples used in this investigation were low-density (0.92 g./cc.) polyethylene films produced by a high pressure process. These polyethylene films (0.2 mm. thickness) were 3.6×10^6 of an average molecular weight and did not contain any antioxidant. Carbonyl and unsaturated compounds used were commercially available materials. Gas-phase graft polymerization was carried out by the in-source γ -irradiation technique

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as follows: polymer films were placed in a stainless-steel autoclave of 20 mm. diameter and 30 cc. volume, and after sufficient evacuation, unsaturated and carbonyl compounds were introduced to the autoclave.

The autoclave were irradiated by γ -rays from a Co^{60} source with a dose rate of 0.13 Mrad./hr. at room temperature. Irradiation *in vacuo* and grafting reaction of only carbonyl compounds were performed in the usual way with glass ampules. After standing for approximately 72 hours, the grafted films were dried to constant weights under vacuum and the IR spectra were recorded with a Nippon-Bunko model DS-403G infrared spectrophotometer using NaCl optics.

The assignment of the absorption bands in the IR spectrum of polyethylene is as follows: in the carbonyl region of $1800\sim 1675\text{ cm}^{-1}$ the absorption band centered at 1733 cm^{-1} has been assigned³⁾ to the aldehyde type carbonyl ($\text{R}-\text{C}\begin{array}{l} \text{O} \\ // \\ \text{H} \end{array}$), 1721 cm^{-1} to the ketone ($\text{R}-\text{C}\begin{array}{l} \text{O} \\ // \\ \text{R}' \end{array}$) and 1712 cm^{-1} to the acid ($\text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\text{OH}$). In the unsaturation region of $1000\sim 800\text{ cm}^{-1}$, 964 cm^{-1} has been assigned⁴⁾ to the *trans*-vinylene unsaturation ($\text{RCH}=\text{CHR}'$), 908 cm^{-1} to the terminal vinyl ($\text{RCH}=\text{CH}_2$) and 888 cm^{-1} to the vinylidene ($\text{RR}'\text{C}=\text{CH}_2$).

By using the values of the respective coefficient ϵ , the amount of unsaturated or carbonyl groups combined with polymers can be calculated from the equation (1.1), which is based upon the Lambert-Beer law.

$$[\text{Numbers of groups}/1000\text{ Carbons}] = (12/\epsilon) [(1/d \cdot l \times \log_{10}(I_0/I))] \quad (1.1)$$

where l is the thickness in cm., d is the density at 20°C . in g./cc., and $\log_{10}(I_0/I)$ is the optical density measured from the base line. The coefficient ϵ for carbonyl groups was given by the calibration curve with the model compounds. For different types of carbonyl groups, the following expression from eq. (1.1) were applied:

$$(\text{RC}\begin{array}{l} \text{O} \\ // \\ \text{OH} \end{array})/1000\text{C} = 2.67 \times 10^{-2} K'_{1712} \quad (1.2)$$

$$(\text{R}\begin{array}{l} \text{O} \\ // \\ \text{R}' \end{array})/1000\text{C} = 6.61 \times 10^{-2} K'_{1721} \quad (1.3)$$

$$(\text{R}-\text{C}\begin{array}{l} \text{O} \\ // \\ \text{H} \end{array})/1000\text{C} = 8.68 \times 10^{-2} K'_{1733} \quad (1.4)$$

where $K' = (1/d \cdot l) \log_{10}(I_0/I)$, and for these of unsaturated groups, the following equations presented by Cernia⁴⁾ could be used:

$$(\text{RCH}=\text{CH}_2)/1000\text{C} = 9.9 \times 10^{-2} K'_{908} \quad (1.5)$$

$$(\text{RCH}=\text{CHR}')/1000\text{C} = 14.0 \times 10^{-2} K'_{964} \quad (1.6)$$

$$(\text{RR}'\text{C}=\text{CH}_2)/1000\text{C} = 11.6 \times 10^{-2} K'_{888} \quad (1.7)$$

The total concentration of carbonyl groups was obtained as the sum of the concentration of the aldehyde type, the ketone type, and the acid type of carbonyl groups, and the total of unsaturated groups is the sum of the *trans*-vinylene, the terminal vinyl and the vinylidene unsaturation.

III. RESULTS AND DISCUSSION

III. 1. 1. γ -Ray Irradiation of Polyethylene Films in Vacuum or in Air

Changes in the IR spectra of polyethylene films irradiated *in vacuo* or in air at a variety of doses were investigated as the fundamentals of γ -ray-induced graft reaction of the polymers. The concentration of unsaturated and carbonyl groups are plotted against irradiation doses in Fig. 1-a), and b).

It is approved that little change in the concentration of carbonyl groups in the

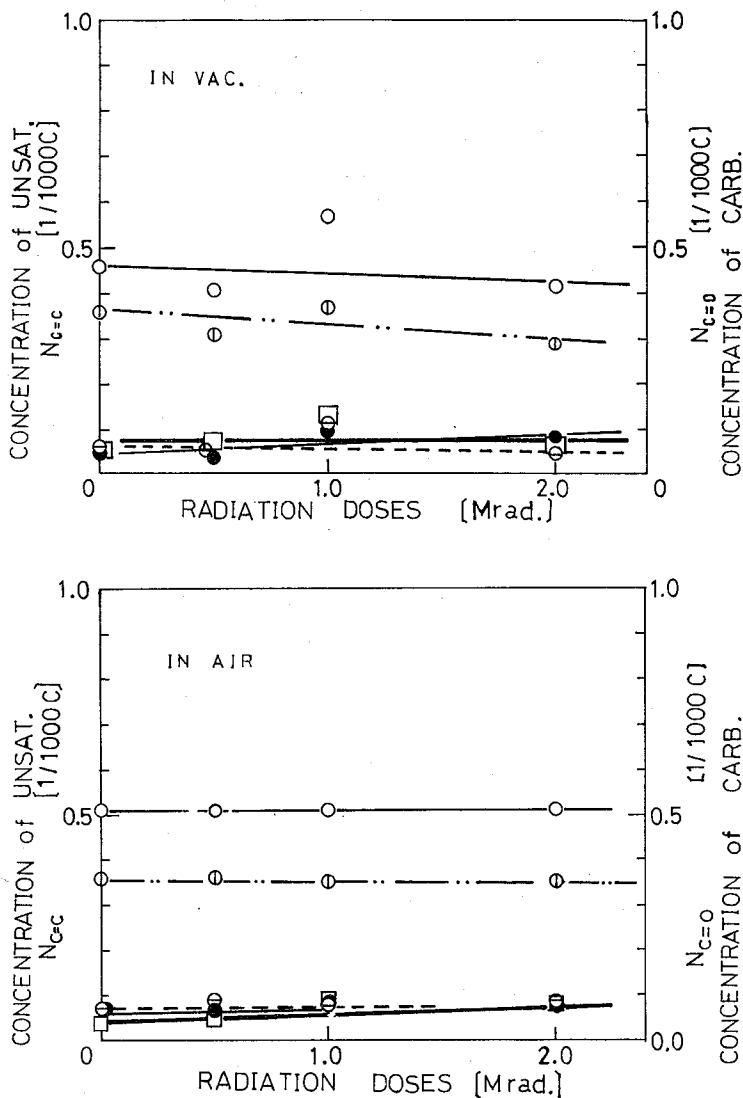


Fig. 1. Concentration of various combined functional groups in polyethylene films irradiated *in vacuo* or in air, \square Total carbonyl groups, \circ Total unsaturated groups, \ominus *trans*-vinylene, \bullet terminal vinyl, \oplus vinylidene, 2-a) irradiated in vacuo 2-b) irradiated in air

Table 1. Changes in the amount of combined butadiene with irradiation doses in the graft polymerization with polyethylene.

Compound	Irradiation dose Mrad.	Degree of Graft Polymerization		Carbonyl groups Total	Unsaturated group			Total	$\frac{RCH=CH_2}{RCH=CHR'}$
		G	%		RCH=CHR'	RCH=CH ₂	RR'C=CH ₂		
Unirradiation	—	—	—	0.05	0.07	0.07	0.34	0.47	1.0
Butadiene (1.5 atm. gauge)	0.13	0.2		0.05	0.36	0.17	0.33	0.86	0.47
	0.5	1.1		0.06	1.53	0.54	0.34	2.41	0.35
	1.0	1.7		0.05	2.64	0.94	0.34	3.92	0.37
	2.0	4.9		0.07	8.08	3.09	0.35	11.52	0.38
Vacuum	0.5	0.0		0.05	0.09	0.08	0.31	0.48	0.94
Air	0.5	0.0		0.09	0.09	0.07	0.36	0.52	0.78

Sample of low-density polyethylene films (0.2 mm. thickness, no antioxidant) Irradiation by Co⁶⁰ γ -rays (0.13 Mrad./hr.) at room temperature

Table 2. Concentration of unsaturated and carbonyl groups in polyethylene films at γ -ray radiation-induced graft polymerization of carbonyl compounds.

Carbonyl Compound (6.7 cc./l.)	Degree of Graft Polymerization		Composition, (numbers/1000 C)							
			Carbonyl groups			Unsaturated groups				
			G	%	$\begin{matrix} O \\ \\ RC-H \end{matrix}$	$\begin{matrix} O \\ \\ RCR' \end{matrix}$	$\begin{matrix} O \\ \\ RC-OH \end{matrix}$	Total	RCH=CHR'	RCH=CH ₂
Unirradiated	—	—	0.01	0.01	0.03	0.05	0.07	0.07	0.34	0.47
Acetone	0.0		0.01	0.02	0.01	0.04	0.05	0.06	0.34	0.45
Hexachloroacetone	0.0		0.00	0.02	0.01	0.03	0.05	0.07	0.33	0.45
Methylvinylketone	1.2		1.98	4.42	1.52	7.92	0.63	0.06	0.20	0.89*
Cyclohexanone	0.0		0.01	0.02	0.01	0.04	0.07	0.10	0.37	0.58
Acetaldehyde	0.0		0.01	0.04	0.03	0.08	0.12	0.10	0.32	0.54
Acrolein	4.3		0.61	1.49	0.77	2.86	0.09	0.09	0.13	0.31*
Acetylchloride	0.0		0.01	0.04	0.06	0.11	0.06	0.08	0.24	0.38

* The band heads of unsaturated groups did not exhibit sharp profile

Sample of low-density polyethylene films (0.2 mm. thickness, no antioxidant) Irradiation by Co⁶⁰ γ -rays (0.13 Mrad./hr.) with a dose of 0.5 Mrad. at room temperature

polyethylene occurred in the course of the standing after irradiation *in vacuo*, and the concentration of terminal vinyl unsaturation increased. While in the case of immediate introduction of air to the *in-vacuo*-irradiated polyethylene films, the concentration of carbonyl groups increased gradually, still the concentration of terminal vinyl showed a constant value lower than that in the case of the standing. Irradiation of polyethylene in air brought about the slight increase in the concentration of carbonyl groups with an irradiation dose, though almost no change in that of terminal vinyl unsaturation was observed.

From these results, it is supposed that the radicals, formed by irradiation *in vacuo*, disappeared during the standing with the cleavage reaction which brought about the formation of terminal vinyl unsaturation, and when the *in-vacuo*-irradiated polyethylene came into contact with air immediately, the formed radicals reacted with oxygen to form carbonyl groups.

III. 1. 2. γ -Ray Radiation-induced Graft Polymerization of Butadiene

Table 1 shows the amount of butadiene grafted-polymerized to polyethylene by the in-source γ -ray-induced graft polymerization with a dose range of 0.1~2.0 Mrad.

The apparent degree of graft polymerization was obtained from the equation.

$$G \% = (W' - W) \times 10^2 / W \quad (3.1)$$

where W , W' are the initial and final weights of the film, respectively.

These results show that the degree of graft polymerization and both the concentration of *trans*-vinylene and terminal vinyl unsaturation increased with an irradiation dose. The ratio of terminal vinyl to *trans*-vinylene corresponds to the selectivity of the addition of *trans*-1.4 and 1.2 of butadiene was about 0.35 independently with the reaction time.

No gel-fraction by the extracting of the butadiene grafted polyethylene films with boiling xylene indicates that cross-linking did not occur in the reaction.

III. 1. 3. γ -Ray Radiation-induced Graft Polymerization of Carbonyl Compounds

The result of the graft polymerization of various carbonyl compounds to polyethylene was shown in Table 2. It proved that polyethylene reacted slightly with saturated carbonyl compounds such as acetaldehyde or acetone, and halogenated carbonyl compounds such as hexachloroacetone or acetylchloride. A large value of the degree of graft polymerization was acquired with unsaturated compounds such as acrolein or methylvinylketone.

In the IR spectrum of an acrolein grafted polyethylene film shown in Fig. 2, new strong bands were observed at 3400 cm^{-1} , at $1800 \sim 1675 \text{ cm}^{-1}$ assigned to carbonyl bands, and in the region of $1300 \sim 800 \text{ cm}^{-1}$. Based upon the similarity to the IR spectrum of an acrolein homopolymer⁵⁾, it is supposed that the band at 3400 cm^{-1} can be assigned to a hydroxyl group ($-\text{OH}$) and the bands at $1200 \sim 1100 \text{ cm}^{-1}$ may be attributed to ether-linkage.

From these results, it is assumed that acrolein was graftpolymerized by carbon-oxygen double bond cleavage to form a hydroxyl group and ether-linkage, and the subsequent cross-linking reaction took place at polymer chains.

Table 3. Concentration of unsaturated and carbonyl groups in polyethylene films at γ -ray radiation-induced graft polymerization of the mixture of unsaturated and carbonyl compounds.

Compound		Irradiation dose Mrad.	Degree of Graft Polymerization		Carbonyl groups			Total	
Carbonyl (6.7 cc./l.)	Unsaturated (1.5 atm. gauge)		G	%	Total	RCH=CHR'	RCH=CH ₂		RR'C=CH ₂
	Unirradiated	—	—		0.05	0.07	0.07	0.34	0.47
Acrolien	Acetylene	0.5	13.6		11.95	0.25	0.11	0.12	0.49
"	Methylacetylene	"	0.3		0.20	0.03	0.07	0.32	0.41
"	Allene	"	2.1		0.98	0.08	0.11	0.27	0.45
"	Methylallene	"	0.0		0.08	0.04	0.11	0.36	0.51
"	Butadiene	0.13	0.2		0.38	0.16	0.08	0.36	0.60
		0.5	1.6		2.04	1.56	0.29	0.36	2.20
		0.0	8.9		6.14	5.78	1.45	0.30	7.49
Methylvinylketone	"	0.5	2.0		1.35	2.12	0.46	0.36	2.94
β -propiolactone	"	"	2.5		0.33	3.13	1.12	0.37	4.62
Diketene	"	0.13	0.6		0.23	0.99	0.38	0.35	1.72
		0.5	0.7		0.26	2.36	0.85	0.36	3.55
		1.0	2.9		0.17	3.64	1.19	0.31	5.15
Acetone	"	0.5	0.1		0.22	0.11	0.07	0.30	0.48
Acetaldehyde	"	"	0.1		0.13	1.05	0.39	0.36	1.80
Hexachloroacetone	"	"	0.6		0.40	0.21	0.20	0.34	0.74
Acetylchloride	"	"	0.9		0.69	0.49	0.21	0.31	1.01

Sample of low-density polyethylene films (0.2 mm. thickness, no antioxidant) Irradiation by Co⁶⁰- γ rays (0.13 Mrad./hr.) at 25°C.

Radiation-Induced Graft Reaction of Polyethylene

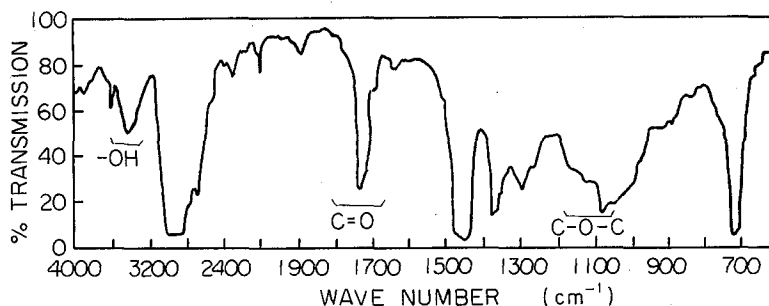


Fig. 2. Infrared spectrum of an acrolein grafted polyethylene film.

III. 1. 4. γ -Ray Radiation-induced Graft Polymerization of the Mixture of Unsaturated and Carbonyl Compounds

The results are shown in Table 3. The degree of graft polymerization and the concentration of carbonyl groups were remarkably increased with the used of the mixture of acetylene and acrolein, while, both the little change in the concentration of unsaturated groups and the formation of the ether-linkage observed in the IR spectrum indicate that acetylene made the amount of combined acrolein accelerated.

Considering the remarkable accelerating effect of acetylene on the γ -radiation-induced cross-linking reaction of polyethylene⁶⁾, the addition of acetylene brought about depressing the disappearance of the polymer radicals to lead to accelerate the degree of graft polymerization of acrolein.

On the other hand, the other unsaturated compounds such as methylacetylene, allene and methylallene made decreased. Butadiene was graft-copolymerized with all kinds of carbonyl compounds and gave the extensive increase in the concentration of carbonyl and unsaturated groups. An unsaturated carbonyl compound mixed with butadiene brought about a large amount of combined monomers than saturated one.

The IR spectrum of the graft-copolymerized polyethylene with butadiene-acrolein mixture is shown in Fig. 3. As these resultant films were solved perfectly in boiling xylene, and both the hydroxyl band at 3400 cm^{-1} and the ether-linkage band at $1200\sim 1100\text{ cm}^{-1}$ were not perceived in the IR spectrum, it is considered that the cross-linking reaction was not occurred in the graft copolymerization.

The amount of combined butadiene was increased by the addition of unsaturated

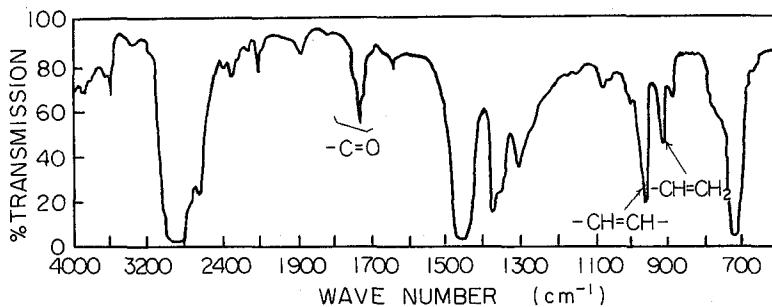


Fig. 3. Infrared spectrum of a butadiene-acrolein grafted polyethylene film.

carbonyl compounds. According to the effect both on the ratio of terminal vinyl to *trans*-vinylene and on the concentration of carbonyl groups, unsaturated carbonyl compounds can be divided into two types: one made the increase in the concentration of unsaturated groups with a constant ratio (0.33~0.39) of terminal vinyl to *trans*-vinylene independently of the experimental conditions, but gave a slight increase in that of carbonyl groups. The other made the decrease in the ratio of terminal vinyl to *trans*-vinylene but gave the increase in the concentration of carbonyl groups. Unsaturated carbonyl compounds such as diketene and β -propiolactone belong to the former and α , β -unsaturated carbonyl compounds such as acrolein and methylvinylketone to the latter.

From these results, the increase in the degree of graft polymerization of butadiene is supposed to be caused by the inhibition of the disappearance of polymer radicals by the added carbonyl compound.

The characteristic phenomenon in the latter graft copolymerization is that the ratio of terminal vinyl to *trans*-vinylene decreased with the molar ratio of the unsaturated carbonyl compound to butadiene in the mixture. This fact shows that an α , β -unsaturated carbonyl compound copolymerized with butadiene accelerated the isomerization of the vinyl type polymer radical to *trans*-vinylene.

A detailed study of the role of α , β -unsaturated carbonyl compounds in the marked acceleration of the radiation-induced graft reaction of polyethylene in the presence of acetylene or 1, 3-butadiene will be reported in a subsequent paper.

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