Role of the unsaturated group in the radiation-induced crosslinking of polyethylene in the presence of chlorotrifluoroethylene

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The effect of unsaturated groups on the crosslinking of polyethylene in the presence of chlorotrifluoroethylene (CTFE) has been studied. Butadiene- and isoprene-grafted polyethylenes with high concentrations of unsaturated groups were crosslinked more markedly than the original polyethylenes. The rate of gel formation increased with the increase in the initial concentration of unsaturated group in polyethylenes, while the rate of grafting of CTFE decreased. The concentration of unsaturated group decreased rapidly during the course of the reaction. The rate of decrease in each unsaturated group was in the order, vinylidene > vinyl > *trans*-vinylene. In the irradiation of polyethylene with a high concentration of unsaturated groups in CTFE, the number of grafted monomers was almost equal to the decrease in numbers of the unsaturated group. These results are discussed in relation to the reaction mechanism and the estimated activation energy of the elementary reaction

INTRODUCTION

In a previous paper[1], it was found that the crosslinking of polyethylene was promoted by the presence of fluorine-containing monomers, especially chlorotrifluoroethylene (CTFE), and the unsaturated groups in polyethylene decreased predominantly with the progress of both the crosslinking of polyethylene and the grafting of the monomer onto polyethylene.

The purpose of the present work is to make clear the role of the unsaturated group in the radiation-induced crosslinking of polyethylene in the presence of CTFE. Polyethylenes with various concentrations of unsaturated group were prepared by the grafting of butadiene and isoprene. Relations among the gel fraction, the degree of grafting of CTFE and the concentration of unsaturated group were studied by γ-ray irradiation in the presence of gaseous CTFE. On the basis of the results, the role of the unsaturated group in the crosslinking of polyethylene in CTFE is discussed.

EXPERIMENTAL

Chlorotrifluoroethylene (CTFE) was used as supplied from Daikin Kogyo Co. Ltd (purity ⩾ 99.5%). Films of low density polyethylene (LDPE) (Sumikathene, number average molecular weight 2.0 x 10^4, density 0.92) and a high density sample (HDPE) (Hizex, 1.4 x 10^5, 0.96) were used in the experiment.

Polyethylene films with a high concentration of unsaturated group were prepared without gel formation of polyethylene by the radiation-induced grafting of butadiene and isoprene at an irradiation dose lower than 2.0 Mrad using the same method as reported previously[2]. The degree of grafting of these monomers was lower than 10 wt %. Since

grafting onto the polyethylene films (thicknesses, 20, 30 and 40 μm) was not affected by the film thickness, the graft chains are considered to be dispersed uniformly throughout the films in the amorphous region.

The i.r. spectrum of the polymer was observed with a Nippon Bunko Model DS-403G infra-red spectrometer. The concentration of the unsaturated group (number of unsaturated groups per 1000 carbons) was determined from the absorbances at 966 (*trans*-vinylene), 910 (vinyl) and 890 (vinylidene) cm^{-1} in the i.r. spectra[3]. The total concentration of unsaturated groups ($[U]_0$), and the concentrations of *trans*-vinylene ($[Ut]_0$), vinyl ($[Uv]_0$) and vinylidene ($[Ud]_0$) groups in polyethylenes are shown in *Table 1*.

The crosslinking was carried out as follows. About 0.1 g of polyethylene film was placed in a glass ampoule of 30 mm diameter and 200 mm long. Gaseous CTFE at a pressure of 1 atm was introduced into the ampoule after evacuation.

The ampoule was irradiated by γ-rays with a ^{60}Co source at a dose rate of 0.05 Mrad/h at room temperature. After the irradiation was completed, the surface of the sample was wiped with a soft cloth, wetted with acetone, dried under vacuum at 40°C for 10 h and then weighed. The degree of grafting (Dg) was determined by the equation (1):

$$Dg = \frac{W_g - W_0}{W_0} \times 100\,(\%) \tag{1}$$

where W_0 and W_g are the weight of the samples before and after irradiation, respectively.

The polyethylene film thus obtained was packed in a 100 mesh stainless steel basket, extracted with hot *p*-xylene in a Soxhlet extractor for 48 h, washed with acetone for 4 h in the same type of extractor, dried in vacuum for 20 h

Table 1 Polyethylene film samples (thickness 20 μm) used in the experiment

Polyethylene sample		No. of unsaturated group 1000 carbons			
		$[U]_0$	$[Ut]_0$	$[Uv]_0$	$[Ud]_0$
Low density polyethylene (LDPE)		0.41	0.06	0.21	0.14
High density polyethylene (HDPE)		0.18	0.00	0.11	0.07
Butadiene-grafted low density polyethylene (BG-LDPE)	BGL-1	1.32	0.93	0.35	0.04
	BGL-2	4.22	3.19	1.00	0.03
	BGL-3	7.54	5.59	1.88	0.07
	BGL-4	9.25	6.76	2.40	0.09
	BGL-5	10.81	7.96	2.81	0.04
Butadiene-grafted high density polyethylene (BG-HDPE)	BGH-1	1.93	1.40	0.50	0.03
	BGH-2	4.77	3.52	1.21	0.04
	BGH-3	9.16	6.77	2.39	0.03
	BGH-4	17.75	13.40	4.29	0.06
Isoprene-grafted low density polyethylene (IG-LDPE)	IGL-1	0.40	0.07	0.14	0.19
	IGL-2	0.63	0.04	0.28	0.31
	IGL-3	0.98	0.05	0.43	0.50
	IGL-4	1.91	0.04	0.93	0.98
Isoprene-grafted high density polyethylene (IG-HDPE)	IGH-1	0.47	0.00	0.17	0.30
	IGH-2	1.15	0.00	0.48	0.67
	IGH-3	1.56	0.00	0.66	0.90
	IGH-4	3.17	0.00	1.40	1.77

groups with the irradiation dose. As shown in *Figure 1*, the rates of gel formation in the presence of CTFE were remarkably higher than those in vacuum. In the irradiation in CTFE, the rates of gel formation of butadiene- and isoprene-grafting polyethylenes were much higher than those of original samples. The order in the rate of gel formation agreed with the order found for the initial total concentration of unsaturated groups $[U]_0$ (*Table 1*).

Grafting rates of CTFE onto butadiene- and isoprene-grafted polyethylenes was markedly lower than those onto original samples (*Figure 2*). The grafting rates in every case increased with the progress of reaction as found for bulk polymerization of this monomer[4].

The total concentration of unsaturated group [U] in butadiene- and isoprene-grafted polyethylenes decreased predominantly with the irradiation dose (*Figure 3*). The initial rate of decrease of unsaturated group in the irradiation in CTFE was about 10 times higher than that *in vacuo*.

Figure 2 Plots of Dg against irradiation dose. Symbols are the same as in *Figure 1*
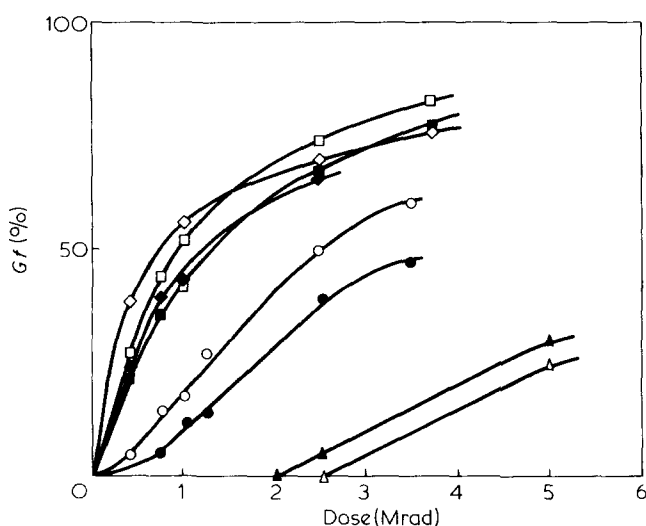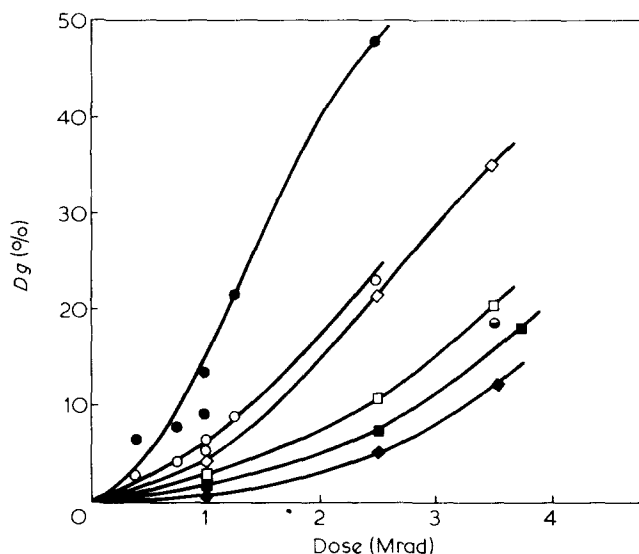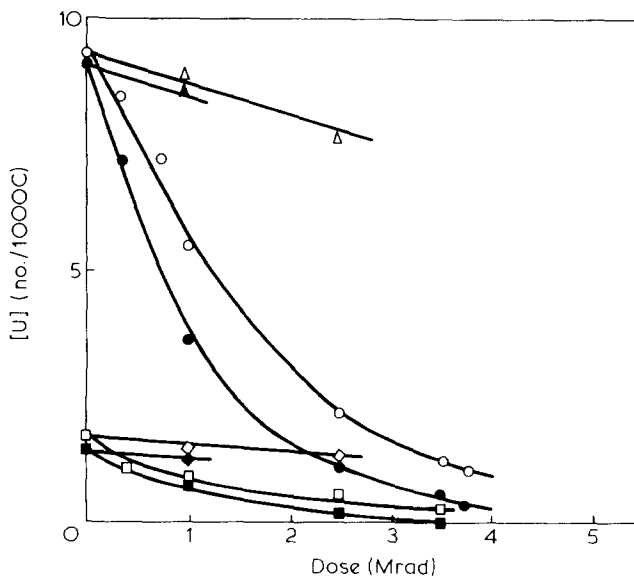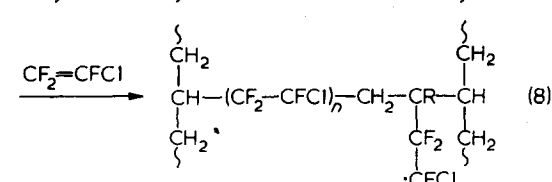

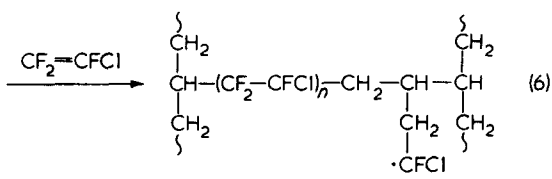*Figure 1* Plots of Gf against irradiation dose. Symbols: irradiation in CTFE: ●, HDPE; ○, LDPE; ◇, BGH-3; □, BGL-4; ■, IGH-2; ◆, IGL-3. Irradiation *in vacuo*, ▲, HDPE; △, LDPE

at 40°C and then weighed. The gel fraction (*Gf*) of the irradiated polyethylene was determined from the weight change during extraction:

$$Gf = \frac{W_a}{W_b} \times 100 \; (\%) \qquad (2)$$

Where W_b and W_a are the weight of the samples before and after extraction.

RESULT AND DISCUSSION

Effect of unsaturated group

Figures 1—3 show the changes in the gel fraction, degree of grafting of CTFE and total concentration of unsaturated
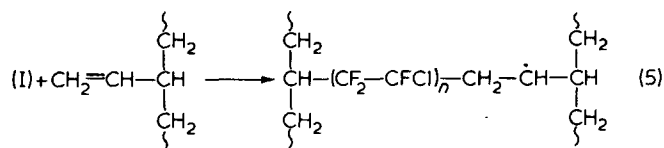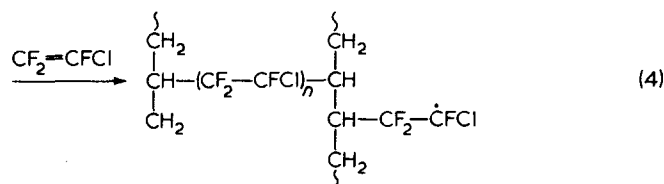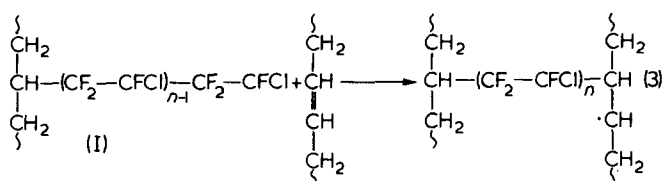

Figure 3 Plots of [U] against irradiation dose. Symbols: irradiation in CTFE: ●, BGH-3; ○, BGL-4; ■, IGH-2; □, IGL-3. Irradiation in vacuum: ▲, BGH-3; △, BGL-4; ◆, IGH-2; ◇, IGL-3

Figure 4 shows the plots of gel fraction and degree of grafting against total initial concentration $[U]_0$ of unsaturated groups of butadiene- and isoprene-grafted polyethylenes. The gel fraction increased with the initial total concentration of unsaturated group, while the degree of grafting decreased. The degree of grafting onto isoprene-grafted polyethylene decreased with the initial concentration of unsaturated group more markedly than that onto butadiene-grafted polyethylene. Gel formation curves were similar for both butadiene- and isoprene-grafted polyethylenes.

Mechanism of crosslinking

Based on the results, it was considered that the addition reactions of propagating graft chain radical to the unsaturated groups in polyethylene [crosslinkings, equations (3), (5) and (7)] and the additions of monomer to the polyethylene radicals produced by the crosslinking reactions [re-initiations, equations (4), (6) and (8)] take place as well as the elementary reactions in the graft polymerization of CTFE, such as initiation, propagation and termination, during irradiation in CTFE.
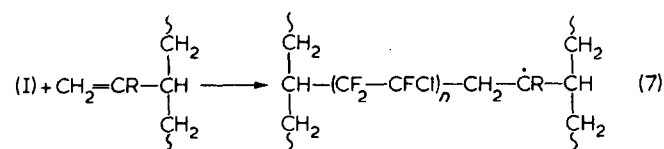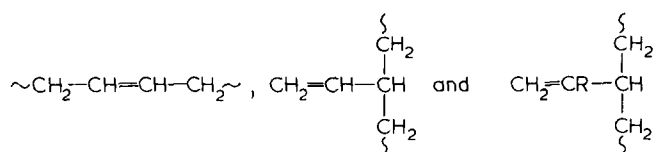
denote respectively, *trans*-vinylene, vinyl and vinylidene groups contained in grafted side chains of polybutadiene and polyisoprene or in a polyethylene chain. R is an alkyl group or polymer chain.

The crosslinkings [equations (3), (5) and (7)] and the re-initiations [equations (4), (6) and (8)] should occur more frequently in the case of polyethylenes with higher concentrations of unsaturated group. The occurrence of these reactions brings about the increase in the rate of gel formation and the decrease in the grafting rate as found in *Figure 4*.

In the irradiation of butadiene-grafted polyethylene, reactions (3), (4), (5) and (6) take place, while, in that of isoprene-grafted samples reactions (5), (6), (7) and (8) occur. Therefore, the difference between the effects of unsaturated groups on the irradiations of butadiene- and isoprene-grafted polyethylenes were considered to be caused by the difference of the reactivities of three types of unsaturated group as discussed in a later section.
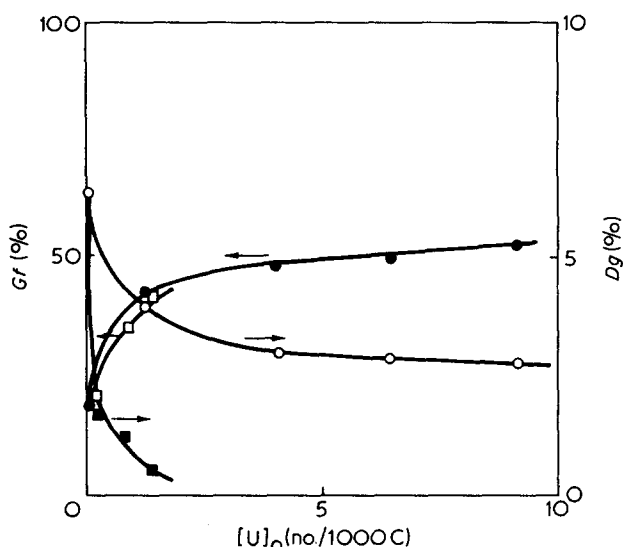

Figure 4 Plots of Gf and Dg against $[U]_0$. Symbols: ●, Gf of BG-LDPE; □, Gf of IG-LDPE; ○, Dg onto BG-LDPE; ■, Dg onto IG-LDPE
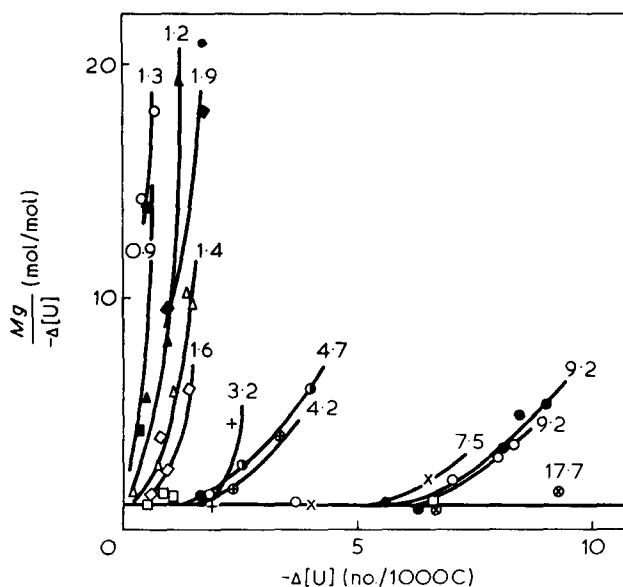

Figure 5 Relation between $Mg/(-\Delta[U])$ and $-\Delta[U]$. Symbols: ◆, BGH-1; ○, BGH-2; ●, BGH-3; ⊗, BGH-4; ○, BGL-1; ⊕, BGL-2; x, BGL-3; ○, BGL-4; □, BGL-5; ▲, IGH-2; ◇, IGH-3; +, IGH-4; □, IGL-3; △, IGL-4
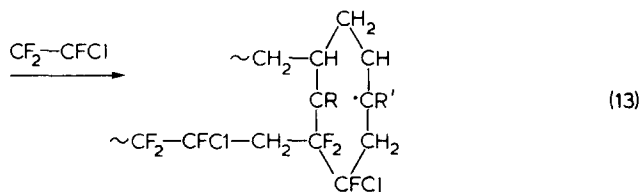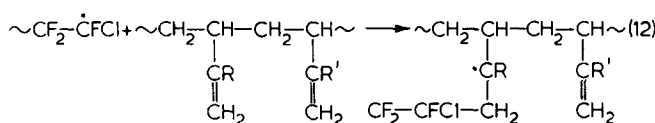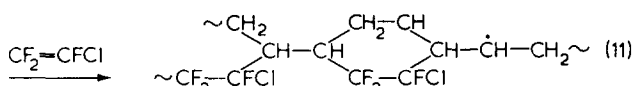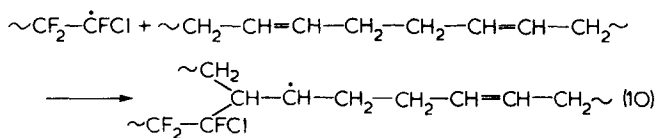
where

Relation between grafting and crosslinking

Since the crosslinking reactions (3), (5) and (7) bring about the decrease in the number of unsaturated groups, the relative frequencies of occurrence of grafting and crosslinking can be discussed by the ratio of the amount of grafted monomer (Mg) to the amount of decrease of unsaturated group ($-\Delta[U]$) represented by equation (9):

$$-\Delta[U] = [U]_0 - [U] \tag{9}$$

In the case of the polyethylene with a low concentration of unsaturated groups, the ratio $Mg/(-\Delta[U])$ increased rapidly with the decrease in the concentration of unsaturated groups during irradiation. In the early stages of the reaction using polyethylene with a high concentration of unsaturated groups the ratio was unity.

These results show that initiation or re-initiation and crosslinking take place almost alternately in the case of polyethylene with a high concentration of unsaturated groups and that propagation also occurs frequently at low concentrations of unsaturated groups. Since the differences between the e values (in the $Q-e$ scheme) of CTFE (e value, 1.49[5]) and olefins containing vinyl, *trans*-vinylene and vinylidene groups (e values, -0.78 for propylene, -2.0 for *trans*-butene-2 and -0.96 for iso-butene[5]) are remarkably large, it is considered that CTFE monomer and the unsaturated groups tend to copolymerize alternately. Along with the alternate crosslinking reaction, cyclizations by alternate reactions may also take place along a side chain composed of polybutadiene or polyisoprene [reactions (10)–(13)].

$\sim CF_2-\overset{\cdot}{C}FCl + \sim CH_2-CH=CH-CH_2-CH_2-CH=CH-CH_2\sim$

$$\longrightarrow \quad \underset{\sim CF_2-CFCl}{\overset{\sim CH_2}{\diagdown}}CH-\overset{\cdot}{C}H-CH_2-CH_2-CH=CH-CH_2\sim \quad (10)$$

$$\underset{\longrightarrow}{CF_2=CFCl} \quad \underset{\sim CF_2-CFCl}{\overset{\sim CH_2}{\diagdown}}CH-CH\underset{CF_2-CFCl}{\overset{CH_2-CH}{\diagdown}}CH-\overset{\cdot}{C}H-CH_2\sim \quad (11)$$

$\sim CF_2-\overset{\cdot}{C}FCl + \sim CH_2-CH-CH_2-CH\sim \longrightarrow \sim CH_2-CH-CH_2-CH\sim (12)$

where R and R' are H or alkyl group.

As shown in *Figure 6*, the ratio $Mg/(-\Delta[U])$ was unity at a value of [U] larger than about 3.5 for butadiene-grafted polyethylene and about 1.5 for isoprene-grafted sample. These results lead to the conclusion that the alternating addition reactions of CTFE with unsaturated groups take place in ranges higher than these values of [U]. The difference in the limited values of [U] of butadiene- and isoprene-grafted polyethylenes is caused by the difference in the reactivities of unsaturated groups as described in the next section.

Reactivity of each unsaturated group

The decrease in number of each unsaturated group was plotted against the degree of grafting of CTFE in the irradiation of butadiene- and isoprene-grafted polyethylenes in the presence of CTFE (*Figure 7*). Data for both butadiene- or isoprene-grafted LDPE and HDPE fall on the same curve as shown in the Figure. The rate of decrease in each unsaturated group was in the order, vinylidene > vinyl > *trans*-vinylene.

In order to study the kinetics of the reaction of solid polyethylene with gaseous CTFE, the effect of monomer diffusion in the polymer was investigated. The irradiations of original LDPE and butadiene- and isoprene-grafted LDPE in the presence of CTFE were carried out using polyethylene films of different thicknesses (20, 30 and 40 μm). As summarized in *Table 2*, the degree of grafting, the gel fraction and the concentration of unsaturated group in polyethylene were not affected by the thickness of the films

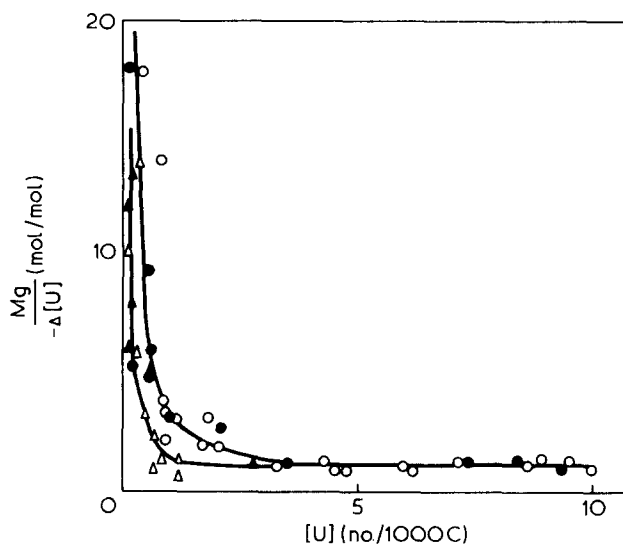*Figure 6* Relation between Mg/(−Δ[U]) and [U]. Symbols: ●, BG-HDPE; ○, BG-LDPE; ▲, IG-HDPE; △, IG-LDPE
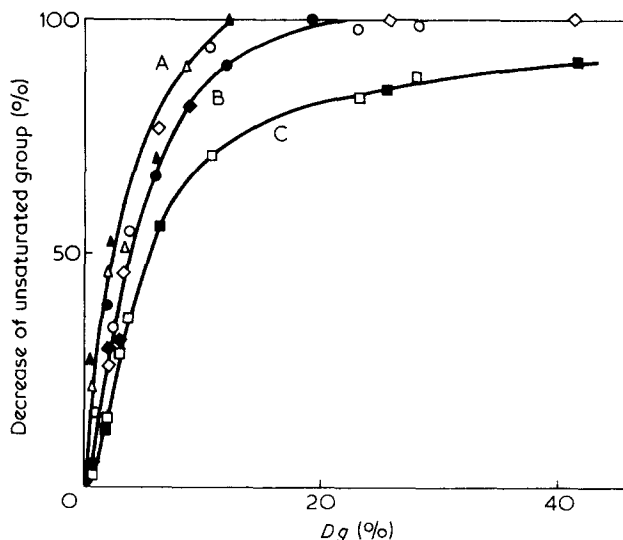

Figure 7 Decrease of each unsaturated group vs. Dg. Symbols: *trans*-vinylene (■) in BGH-3 and (□) in BGL-4; vinyl (◇) in BGH-3, (○) in BGL-4, (◆) in IGH-2 and (●) in IGL-3; vinylidene (▲) in IGH-2 and (△) in IGL-3. A, Vinyldiene; B,vinyl; C, *trans*-vinylene

Table 2 Irradiation of polyethylene films with different thicknesses in the presence of CTF[a]

Sample	Thickness (μm)	No. of unsaturated group 1000 carbons				Dg (%)	Cf (%)	No. of unsaturated group 1000 carbons			
		$[U]_0$	$[Ut]_0$	$[Uv]_0$	$[Ud]_0$			$[U]$	$[Ut]$	$[Uv]$	$[Ud]$
LDPE	20	0.41	0.06	0.21	0.14	24.2	54.4	0.01	0.01	0.00	0.00
	30	0.41	0.06	0.21	0.14	23.4	53.2	0.02	0.01	0.01	0.00
	40	0.41	0.06	0.21	0.14	23.6	53.9	0.01	0.01	0.00	0.00
BG-LDPE[b]	20	15.88	11.82	4.03	0.03	2.9	52.8	10.54	8.40	2.14	0.00
	30	15.24	11.00	4.12	0.02	3.0	57.6	10.91	8.61	2.30	0.00
	40	15.55	11.51	3.92	0.02	2.7	54.0	11.13	8.92	2.21	0.00
IG-LDPE[c]	20	2.83	0.02	1.21	1.60	0.6	46.3	1.34	0.02	0.62	0.70
	30	2.71	0.04	1.14	1.53	0.7	45.2	1.26	0.02	0.58	0.66
	40	2.81	0.03	1.16	1.62	0.6	47.4	1.32	0.03	0.62	0.68

[a] Reaction conditions: temperature; about $20°C$, monomer pressure; 1 atm., irradiation dose; 2.5 Mrad for LDPE and 1.0 Mrad for BG-LDPE and IG-LDPE
[b],[c] Prepared by the radiation-induced grafting of butadiene and isoprene under the following conditions: temperature $\sim 20°C$; monomer pressure 1 atm for butadiene and vapour pressure at the temperature for isoprene; irradiation dose 2.5 Mrad
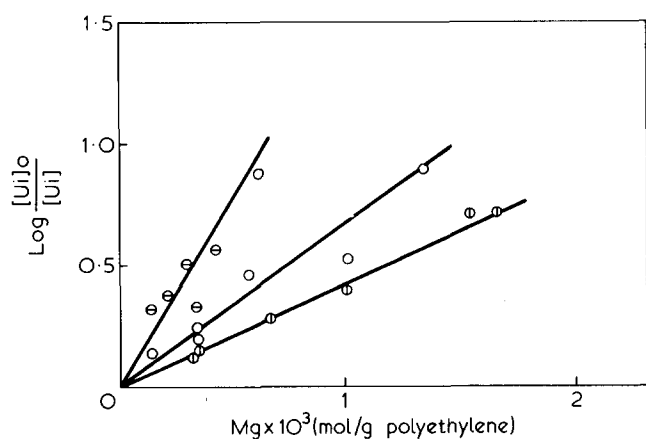

Figure 8 Relation between $\log([Ui]_0/[Ui])$ for each unsaturated group and Mg. A, Vinylidene; B, vinyl; C, *trans*-vinylene

used in this experiment. These results indicate that the crosslinking of polyethylene film in the presence of CTNF is not affected by the monomer diffusion.

Since the concentration of unsaturated group is decreased by the addition reaction with the propagating graft chain radicals [crosslinking reactions (3), (5) and (7)], the rate of decrease of unsaturated group is expressed by equation (13):

$$-\frac{d[Ui]}{dt} = k_{ci}[M \cdot][Ui] \qquad (13)$$

Where, $[Ui]$ is $[Ut]$, $[Uv]$ or $[Ud]$, k_{ci} is the rate constant for each of reactions (3), (5) and (7), $[M \cdot]$ is the concentration of propagating graft chain radical of CTFE and t is the reaction time.

In the diffusion-free monomer reaction the concentration of CTFE ($[M]$) is almost independent of reaction time under low converson of the monomer. Thus, integrating and rearranging equation (13) gives equation (14):

$$\ln \frac{[Ui]_0}{[Ui]} = \frac{k_{ci}}{k_p[M]} \int_0^t k_p[M \cdot][M] \, dt \qquad (14)$$

where $[Ui]_0$ is $[Ut]_0$, $[Uv]_0$ or $[Ud]_0$ and k_p is the rate constant for propagation of CTFE.

On the other hand, the amount of grafted monomer (*Mg*) is given by following equation;

$$Mg = \int_0^t (R_i + k_p[M \cdot][M]) \, dt \qquad (15)$$

where R_i is the rate of the addition reaction of monomer to polyethylene radical (initiation and re-initiation). When $k_p[M \cdot][M]$ is much larger than R_i equation (14) can be written as follows:

$$\ln \frac{[Ui]_0}{[Ui]} = \frac{k_{ci}}{k_p[M]} Mg \qquad (16)$$

The assumption $k_p[M \cdot][M] \gg R_i$ will be valid, when the propagation is predominant compared with crosslinking and re-initiation; the ratio $Mg/(-\Delta[U])$ is thus very large.

The data used for kinetic analysis were obtained in the case $Mg/(-\Delta[U]) > 10$ with monomer conversion $< 6\%$. *Figure 8* shows the linear relationship between the value of $\log([Ui]_0/[Ui])$ for each unsaturated group and *Mg*. The values of $k_{ci}/k_p[M]$ in equation (16) for various unsaturated groups can be obtained from the slopes of the straight lines.

The values of $k_{ci}/k_p[M]$ are summarized in *Table 3*. Since $k_p[M]$ is considered to be constant, these values show the relative reactivities of various unsaturated groups in the crosslinking reactions. From the values of $k_{ci}/k_p[M]$ the reactivities of unsaturated groups were clearly recognized to be in the order: vinylidene $>$ vinyl $>$ *trans*-vinylene.

As reported by Stefani *et al.*[6], the order of the reactivities of unsaturated groups to $\dot{C}F_3$ radical was *trans*-butene-2 (a model *trans*-vinylene compound) $<$ propylene (vinyl) $<$ isobutene (vinylidene) (*Table 3*). The relative reactivities of these olefins agreed well with those of the corresponding unsaturated groups in the radiation-induced crosslinking of butadiene- and isoprene-grafted polyethylenes.

Table 3 Values of k_{ci}/k_p M] of unsaturated group in polyethylene obtained from *Figure 8* and the reactivities of olefins in the addition reaction to trifluoromethyl radical[6]

Reactivity of unsaturated group in polyethylene			Reactivity of olefines to CF_3[6]		
Unsaturated group	k_{ci}/k_p[M] (g-PE/mol)	Relative reactivity	Olefin	k_2/k_1[a]	Relative reactivity
trans-vinylene	4.2×10^2	0.28	*trans*-Butene-2	584	0.34
Vinyl	6.9×10^2	0.46	Propylene	630	0.37
Vinylidene	1.5×10^3	1.0	Iso-butene	1720	1.0

[a] k_1 and k_2 are rate constants of following reactions;

$$\dot{C}F_3 + SH \xrightarrow{\ k_1\ } CF_3H + S\cdot$$

$$CF_3 + RR'C{=}CR''R''' \xrightarrow{\ k_2\ } CF_3{-}\overset{\overset{\displaystyle R}{|}}{\underset{\underset{\displaystyle R'}{|}}{C}}{-}\overset{\overset{\displaystyle R''}{|}}{\underset{\underset{\displaystyle R'''}{|}}{C}}\cdot$$
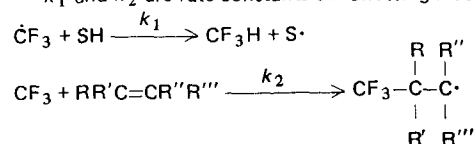
where, SH is 2,3-dimethyl butane and $RR'C{=}CR''R'''$ is olefin

Table 4 Estimated activation energy of each elementary reaction

Reaction	D_i (kcal mol)	D_f (kcal mol)	E (kcal/mol)
Propagation	34.7	66.7	2.56
Crosslinking (3)	50.5	76.2	1.52
(5)	53.0	82.5	0.45
(7)	50.0	82.5	0.45
Reinitiation (4)	34.7	73.6	1.23
(6)	34.7	73.6	1.23
(8)	34.7	67.5	2.35

Energetic consideration of reaction

In order to discuss the results described above in energetic terms, the activation energies of model reactions of propagation, crosslinking and re-initiation (initiation) were calculated.

The activation energies (E) were estimated using the semi-empirical equation (17) proposed by Kagiya et al.[7]:

$$E = \frac{D_i[(1 - 2\kappa)D_f + \kappa^2 D_i]^2}{(D_f - \kappa^2 D_i)^2} \qquad (17)$$

Where, D_i and D_f are, respectively, the dissociation energies of the bonds ruptured and formed in the reaction. The parameter κ in equation (17) is related to the heat of reaction (Q) by the equation (18):

$$\kappa = \exp(\beta Q) \qquad (18)$$

where β is a constant depending on the kind of reaction. The value of β was calculated by equation (19) for an addition reaction to the carbon–carbon unsaturated bond:

$$\beta = \frac{0.001554 D_i}{D_f - 95.0} + 0.03028 \qquad (19)$$

The activation energies thus calculated are listed in *Table 4*. The activation energy of propagation is larger than that of each of the crosslinkings (3), (5) and (7). Therefore, it is considered that the crosslinkings take place more easily than the propagation. In conventional vinyl monomers, such as styrene, methyl acrylate, vinyl acetate and vinyl chloride, the

activation energies of propagations are smaller than those of addition reactions of the unsaturated groups[2]. Furthermore, the activation energies of the crosslinks (3), (5) and (7) in CTFE is much smaller than the activation energies (>4 kcal mol^{-1}) in the addition reactions of propagating radicals for these vinyl monomers. The acceleration effect of CTFE on the crosslinking of polyethylene can be explained by these energetic considerations.

On the other hand, the activation energies for reinitiation are smaller than those calculated for the addition reactions of alkyl radicals to unsaturated groups (2.1–3.8 kcal mol^{-1} for the addition reactions of various unsaturated groups to a secondary carbon radical and 3.4–6.8 kcal mol^{-1} for a tertiary radical).

Therefore, the addition of monomer to polyethylene radical is thought to take place in preference to addition of unsaturated groups. These energetic considerations indicate that the alternate reaction of CTFE with unsaturated groups tends to take place as found in the experimental results.

The activation energies for crosslinking reactions (3), (5) and (7) are in the order, $E(3) > E(5) > E(7)$. This result explains the relative reactivity of each unsaturated group in the crosslinks.

From the activation energies for re-initiation reactions (4), (6) and (8) it was found that the reactivity of the tertiary carbon radical produced by the crosslinking (7) is lower than those of other polyethylene radicals produced by reactions (3) and (5). Therefore, the vinylidene group has the highest reactivity in the crosslinking reaction and the radical produced by the crosslinking has the lowest reactivity in the re-initiation. These considerations are consistent with the results that the rate of grafting of CTFE onto the isoprene-grafted polyethylene containing a vinylidene group is lower than that onto the butadiene-grafted polyethylene.

The activation energies for the abstraction of allyl hydrogen in unsaturated group-containing polyethylene by the propagating graft chain radical were estimated as 7.8–8.2 kcal mol^{-1}. Since the values are much larger than the activation energies of the crosslinking reactions (3), (5) and (7), it was concluded that the degradative chain transfer reaction does not take place so frequently.

The estimated results for activation energies on the basis of the proposed reaction mechanism were consistent with the experimental results in the present work.

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