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### Radiation-Induced Cross-Linking of Polyethylene in the Presence of Various Acetylenic Compounds

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## Radiation-Induced Cross-Linking of Polyethylene in the Presence of Various Acetylenic Compounds

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### ABSTRACT

A study was made on the radiation-induced cross-linking reaction of polyethylene by exposing film samples to  $^{60}\text{Co}$   $\gamma$ -rays in vacuum or in the presence of various acetylenic compounds such as acetylene, its  $\text{C}_2$  to  $\text{C}_3$  higher derivatives, and their mixture with tetrafluoroethylene (TFE). The samples (0.2 mm thick) were found to decrease in weight when irradiated in vacuum, but to increase in the presence of the additives. The IR spectrum measurements of the resultant showed that the trans-vinylene unsaturation increased by the irradiation, especially in the presence of the  $\text{C}_2$  to  $\text{C}_3$  derivatives, and terminal vinyl increased markedly in acetylene. However, the formation of these unsaturations were depressed when the film was irradiated in the mixed gas with TFE. The rate of the cross-linking reaction was accelerated by the

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addition of acetylene-TFE, acetylene, trifluoromethylacetylene, perfluorobutylene-2, perfluorobutyne-2-TFE, and methylacetylene-TFE [ $G(\text{cross-linking}) = 4.4-1.2$ ]. It was reduced with methylacetylene, butyne-1, butyne-1-TFE, pentyne-1, pentyne-1-TFE, pentyne-2, pentyne-2-TFE, [ $G(\text{cross-linking}) = 0.6-0.1$ ]. On the basis of these experimental results a chain reaction scheme of the cross-linking is proposed, and it is discussed on the basis of the activation energy of the elementary reactions.

## INTRODUCTION

It is well known that polyethylene suffers intermolecular cross-linking as a result of the irradiation of ionizing radiation [1]. The efficiency of the reaction, which depends on the chemical structure and the physical state of the polymer, is rather low. The  $G$  value of the cross-linking has been reported to be about 1.0 to 2.5 [2-9]. It was recently found that the cross-linking reaction was markedly promoted in the presence of acetylene [10] or in a mixture of acetylene and tetrafluoroethylene [11]. However, the mechanism of the promotion is not yet clear, and the effect of higher acetylenic derivatives has not been reported.

In this work the cross-linking reaction of polyethylene was investigated by exposing its film samples to  $^{60}\text{Co}$   $\gamma$ -rays in the presence of acetylene or its higher ( $\text{C}_3$  to  $\text{C}_5$ ) derivatives. A study was made of the reactions in the presence of some fluorine-containing derivatives or in mixture of the acetylenic compounds with tetrafluoroethylene.

## EXPERIMENTAL

The polyethylene used was Hizex 2200P, manufactured by the Mitsui Oil Chemical Co. It was molded at  $140^\circ\text{C}$  into a film of about 0.2 mm thickness. The film samples were degassed under  $10^{-4}$  Torr for 15 hr in glass ampules. Irradiation by  $\gamma$ -rays was carried out in vacuum or in atmospheres of  $\text{CH}=\text{CH}$ ,  $\text{CH}=\text{CCH}_3$ ,  $\text{CH}=\text{CC}_2\text{H}_5$ ,  $\text{CH}=\text{CC}_3\text{H}_7$ ,  $\text{CH}_3\text{C}=\text{CC}_2\text{H}_5$ ,  $\text{CH}=\text{CCF}_3$  (TFMA), and  $\text{CF}_3\text{C}=\text{CCF}_3$  (PFB), and mixture of each with tetrafluoroethylene (TFE). These additives, which had been purified by the alternate freezing and thawing technique under reduced pressure, were charged in until the total pressure reached  $2 \text{ kg/cm}^2$  at room temperature. The  $\gamma$ -rays used were from 120,000 Ci of  $^{60}\text{Co}$ , and the irradiation was carried out at room temperature with a constant dose rate of  $1 \times 10^6$  rad/hr for 4 to 130 hr.

The irradiated ampules were allowed to stand in the dark at room temperature for 40 hr before being opened. The film samples were degassed under  $10^{-3}$  Torr for 20 hr and weighed in order to determine the change in weight. Further, they were immersed in boiling xylene for 20 hr and then in methanol for 4 hr, and dried in vacuum for 20 hr at room temperature. The insoluble gel fraction was determined by measuring the weight percent of the residue.

IR spectra of the irradiated polyethylene were measured with a Hitachi-Perkin Elmer IR spectrophotometer, Model 225. Unsaturation content was determined from the absorbance at 966 (trans-vinylene), 910 (terminal vinyl), and 890 (vinylidene)  $\text{cm}^{-1}$  [12].

## EXPERIMENTAL RESULTS

The results of the irradiation in vacuum and in the presence of acetylenic compounds are summarized in Table 1, and those in the cases of added TFE are given in Table 2.

### Change in Weight and Gel Fraction

As can be seen in Tables 1 and 2, the polyethylene films decrease in weight when irradiated in vacuum, but increased in the presence of the additives. The change in weight was not observed when polyethylene was not treated with  $\gamma$ -ray irradiation. The change in gel fraction is illustrated in Fig. 1 as a function of the radiation dose. It is evident that the gel formation is accelerated by the addition of acetylene, acetylene-TFE, TFMA, PFB, PFB-TFE, and methylacetylene-TFE. On the other hand, it is depressed by methylacetylene, butyne-1, butyne-1-TFE, pentyne-1, pentyne-1-TFE, pentyne-2, and pentyne-2-TFE.

### Changes in Polymer Structure

The IR spectra of polyethylene are shown in Fig. 2: nonirradiated, irradiated in acetylene, methylacetylene, and methylacetylene-TFE. The significant difference in these spectra is the fact that the irradiated polyethylene shows new absorption peaks at  $910 \text{ cm}^{-1}$  (terminal vinyl) and  $966 \text{ cm}^{-1}$  (trans-vinylene). As illustrated in Figs. 3 (terminal vinyl), 4a, and 4b (trans-vinylene), the amount of these unsaturations increases almost linearly with the radiation dose. In these IR spectra the formation of the conjugated double bonds ( $1580$  to  $1650 \text{ cm}^{-1}$ ) and the trisubstituted vinylene cannot be found.

TABLE 1. Results of the  $\gamma$ -Ray Irradiation in the Presence of Various Acetylenic Compounds<sup>a</sup>

Additives	Dose (Mrad)	Weight increment (wt%)	Gel fraction (wt%)	Terminal vinyl (No./1000C)	trans-Vinylene (No./1000C)	Vinylidene (No./1000C)
Nonirradiated	-	-	0.0	0.00	0.01	0.06
Vacuum	4.0	-	15.4	0.00	0.11	0.06
	6.0	-0.1	23.2	0.01	0.14	0.06
	16.0	-0.4	45.5	0.00	0.31	0.05
	20.0	-	49.9	0.01	0.41	0.06
Acetylene	4.0	-	59.2	0.07	0.11	0.05
	6.0	0.32	69.2	0.16	0.08	0.03
	16.0	0.70	81.7	0.34	0.27	0.04
	20.0	0.81	83.5	0.48	0.36	0.06
Methyl-acetylene	6.0	0.50	13.9	0.03	0.21	0.03
	16.0	0.70	34.0	0.04	0.49	0.05
	20.0	0.80	44.0	0.05	0.59	0.06
Butyne-1	5.0	0.31	0.9	0.05	0.24	0.06
	16.0	0.60	8.7	0.04	0.50	0.05
	20.0	0.91	15.5	0.03	0.62	0.07
	67.0	-	51.6	0.02	1.07	0.13
	107.5	-	73.6	0.09	1.91	0.14
Pentyne-1	5.0	0.30	1.0	0.00	0.13	0.02
	16.0	-	11.1	0.03	0.44	0.07
	20.0	1.30	9.8	0.04	0.60	0.10
	67.0	-	46.6	0.08	1.64	0.19
	107.5	-	65.3	0.08	2.31	0.18
Pentyne-2	20.0	0.68	0.3	0.00	0.38	0.00
	67.0	-	14.6	0.00	1.03	0.04
	107.5	-	40.9	0.04	1.40	0.04
	128.5	-	47.7	0.05	2.01	0.10

TFMA <sup>b</sup>	4.0	-	7.2	0.07	0.11	0.06
	6.0	-	42.0	0.03	0.16	0.06
	16.0	-	58.3	-	-	-
	20.0	-	66.8	0.07	0.49	0.06
PFBC <sup>c</sup>	4.0	-	30.4	0.01	0.08	0.03
	6.0	-	46.4	0.00	0.08	0.05
	16.0	0.62	57.5	0.00	0.27	0.00
	20.0	1.02	73.0	0.01	0.31	0.03

<sup>a</sup> Conditions: dose rate,  $1 \times 10^6$  rad/hr; temperature,  $\sim 25^\circ\text{C}$ .

<sup>b</sup> TFMA: trifluoromethylacetylene.

<sup>c</sup> PFBC: perfluorobutylene-2.

TABLE 2. Results of  $\gamma$ -Ray Irradiation in the Mixture of Acetylenic Compounds with TFE

Additives <sup>a</sup>	Dose (Mrad)	Weight increment (wt%)	Gel fraction (wt%)	Terminal vinyl (No./1000C)	trans-Vinylene (No./1000C)	Vinylidene (No./1000C)
Acetylene-TFE	4.0	-	76.9	0.10	0.07	0.04
	6.0	1.79	82.2	0.07	0.06	0.02
	16.0	2.41	93.8	-	-	0.01
Methyl acetylene-TFE	20.0	2.53	94.3	0.28	0.39	0.05
	4.0	0.62	25.5	0.00	0.17	0.05
	6.0	-	34.2	0.03	0.22	0.05
Butyne-1-TFE	16.0	-	58.8	0.02	0.39	0.05
	20.0	2.14	66.8	0.05	0.50	0.06
	5.0	0.53	0.8	0.00	0.08	0.07
Pentyne-1-TFE	16.0	1.29	0.7	0.00	0.28	0.05
	20.0	1.62	35.9	0.01	0.55	0.07
	67.0	5.53	67.1	0.03	0.84	0.06
Pentyne-2-TFE	107.5	5.70	80.5	0.01	0.90	0.03
	5.0	0.71	1.6	0.02	0.13	0.00
	16.0	-	11.8	0.02	-	0.06
PFD-TFE	20.0	1.42	15.7	0.04	0.59	0.07
	67.0	5.06	54.3	0.03	0.90	0.09
	107.5	7.85	73.5	0.04	1.53	0.13
PFD-TFE	6.0	0.90	1.2	0.02	0.05	0.05
	20.0	1.42	0.6	0.00	0.34	0.02
	67.0	-	19.9	0.00	1.13	0.07
PFD-TFE	107.5	3.49	48.5	-	-	-
	120.5	5.03	58.0	-	-	-
	6.0	-	43.7	0.00	0.06	0.13
PFD-TFE	16.0	3.20	62.3	0.02	0.20	0.05
	20.0	3.33	63.5	0.02	0.21	0.05

<sup>a</sup>TFE: tetrafluoroethylene.

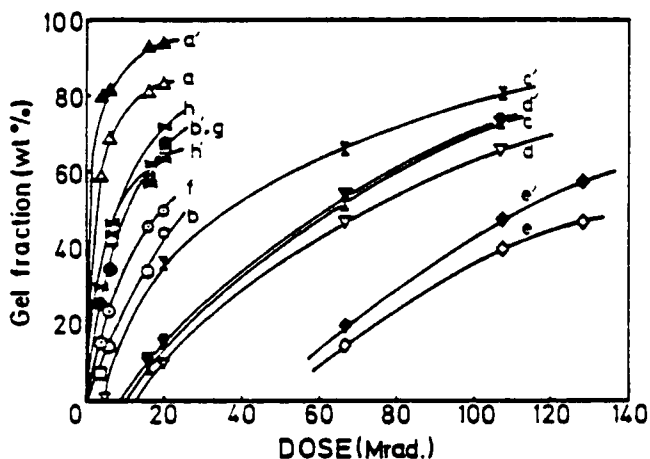


FIG. 1. Gel fraction vs dose in radiation-induced cross-linking in the presence of various acetylenic compounds: (a) acetylene, (b) methylacetylene, (c) butyne-1, (d) pentyne-1, (e) pentyne-2, (f) vacuum, (g) TFMA, and (h) PFB. The primes indicates that the polyethylene was irradiated in the mixed gas of the acetylenic compound with TFE.

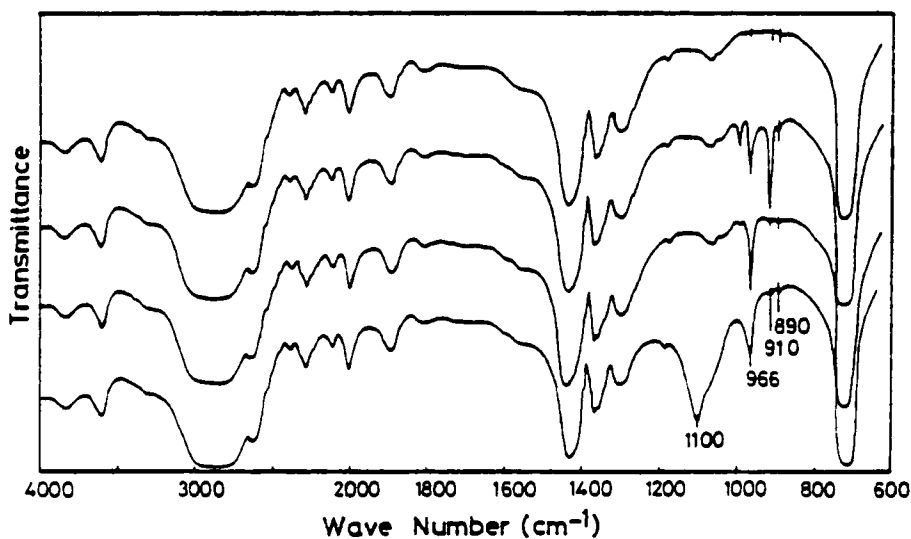


FIG. 2. IR spectra of polyethylene. From the top: Nonirradiated, irradiated in acetylene, methylacetylene, and methylacetylene-TFE.



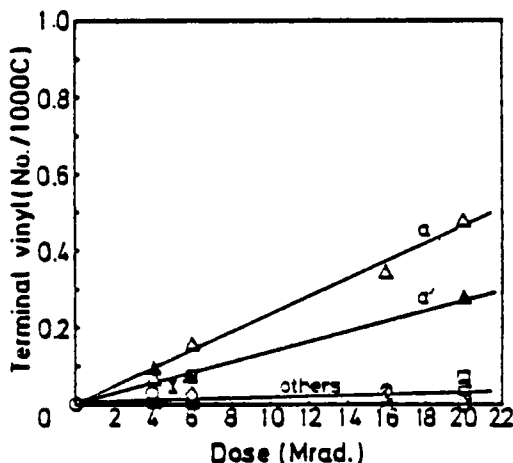


FIG. 3. Formation of terminal vinyl unsaturation in the presence of various acetylenic compounds: (a) acetylene; (a') acetylene-TFE; (others) methylacetylene, butyne-1, pentyne-2, PFB, mixture of each of them with TFE, TFMA, and vacuum.

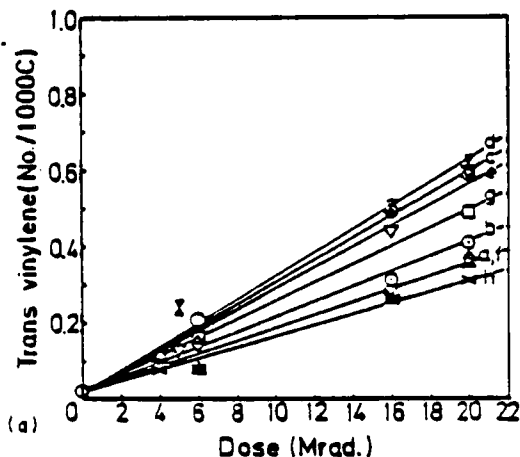


FIG. 4a. Formation of trans-vinylene unsaturation in the presence of various acetylenic compounds: (a) acetylene, (b) methylacetylene, (c) butyne-1, (d) pentyne-1, (e) pentyne-2, (f) vacuum, (g) TFMA, and (h) PFB.

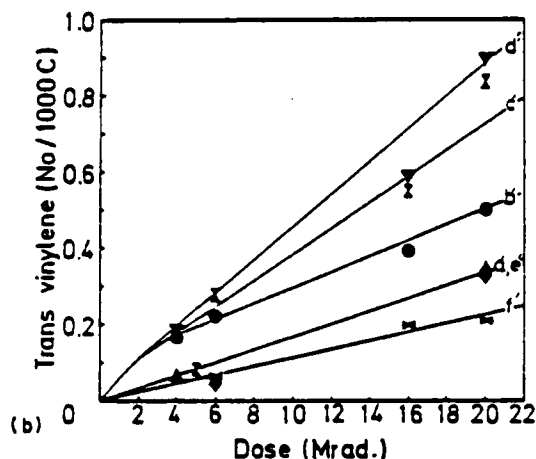


FIG. 4b. Formation of trans-vinylene unsaturation in the presence of the mixed gas of acetylenic compound with TFE: (a') acetylene, (b') methylacetylene, (c') butyne-1, (d') pentyne-1, and (e') pentyne-2, and (f') PFB.

#### G Values of Cross-Linking, Main-Chain Scission, and the Formation of the Unsaturation

By putting  $S$  (sol fraction) =  $1 - (\text{gel fraction})$ ,  $S + S^{1/2}$  was calculated and plotted as a function of reciprocal irradiation dose ( $1/r$ ) (Fig. 5, Charlesby-Pinner's plot [4]). From the slopes and the intercepts of the straight lines obtained, the  $G$  values of the cross-linking and the main-chain scission can be evaluated. The results are summarized in Table 3 together with the  $G$  values of the formation of the unsaturations, which were determined from Figs. 4a and 4b.

By comparing the results, the following facts become evident: 1)  $G(\text{cross-linking})$ ,  $G(\text{scission})$ , and  $G(\text{terminal vinyl})$  increase remarkably, but  $G(\text{trans-vinylene})$  decreases in the acetylene atmosphere. On the other hand, 2)  $G(\text{cross-linking})$  and  $G(\text{scission})$  decrease in the  $C_3$  to  $C_5$  derivatives. 3) In the fluorine-containing derivatives,  $G(\text{cross-linking})$  and  $G(\text{scission})$  increase, and 4), in the mixture of the acetylenic compound with TFE,  $G(\text{cross-linking})$  increases, and  $G(\text{scission})$  and  $G(\text{unsaturation})$  decrease.

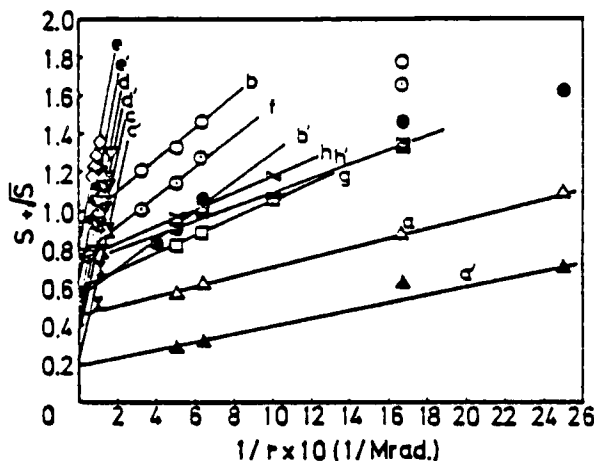


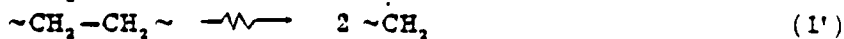
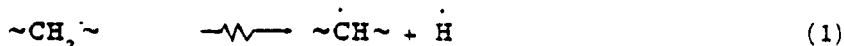
FIG. 5. Charlesby-Pinner's plot: (a) acetylene, (b) methylacetylene, (c) butyne-1, (d) pentyne-1, (e) pentyne-2, (f) vacuum, (g) TFMA, and (h) PFB. The primes indicate that the polyethylene was irradiated in the mixed gas of the acetylenic compound with TFE.

## DISCUSSION

### Proposed Mechanism of the Reaction

Based on the experimental results presented above, we proposed the following chain scheme for the reaction in the presence of acetylenic compounds.

#### Initiation



#### Propagation

Addition of acetylenic compounds:

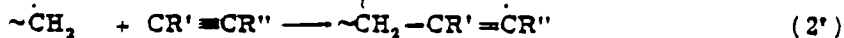
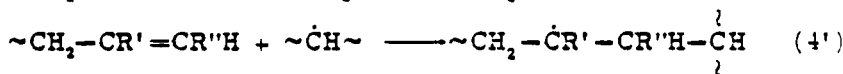
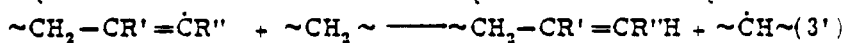
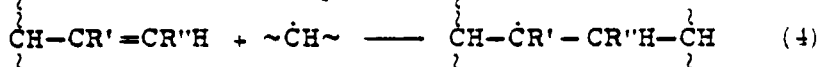
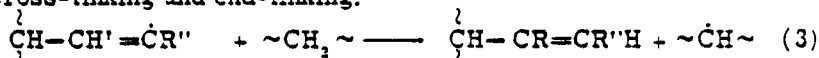


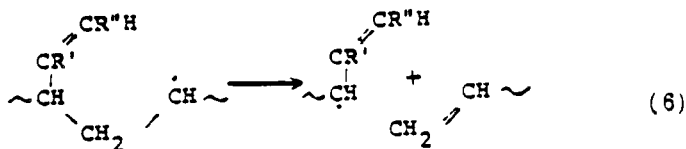
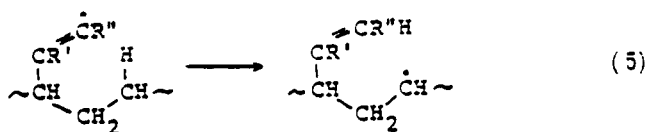
TABLE 3. G Values of Cross-Linking, Main-Chain Scission, and Formation of Unsaturation

Additives	G(cross-linking)	G(scission)	G(terminal vinyl)	G(trans-vinylene)
Acetylene	4.4	4.1	2.0	1.5
Acetylene-TFE	5.0	2.1	1.2	1.5
Methylacetylene	0.6	1.1	0	2.7
Methylacetylene-TFE	1.2	0.8	0	2.5
Butyne-1	0.2	0.1	0	2.8
Butyne-1-TFE	0.2	0.1	0	2.1
Pentyne-1	0.2	0.1	0	2.7
Pentyne-1-TFE	0.2	0.1	0	2.6
Pentyne-2	0.1	0.1	0	1.7
Pentyne-2-TFE	0.1	0.1	0	1.5
TFMA	2.6	3.2	0	2.3
PFB	2.5	3.8	0	1.6
PFB-TFE	2.2	3.9	0	1.1
Vacuum	1.0	1.2	0	1.8

Cross-linking and end-linking:



Main-chain scission:



### Deactivation of vinyl radical



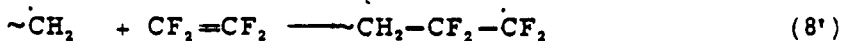
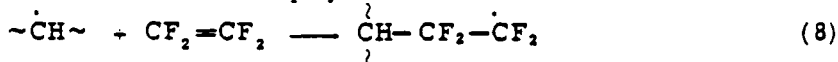
In the above scheme the reaction is initiated by the formation of the polymer radicals resulting from the dissociation of C-H or C-C bonds of polyethylene during  $\gamma$ -ray irradiation. The addition of the acetylenic compounds to the initial polymer radicals is introduced with due consideration of the facts that the weight of polyethylene decreases in vacuum, but that it increases in the presence of the additives. As pointed out in earlier section as typical results, the G(trans-vinylene) decreases in acetylene and the IR spectra of the polymers irradiated in acetylene or methylacetylene (Fig. 2) do not show the existence of conjugated or trisubstituted unsaturations. The absence of trisubstituted unsaturation was also confirmed in the case of TFMA. From these results it may be said that cross-linking through the combination between two vinyl-type radicals, or between the vinyl-type radical and the initial polymer radical, is negligible. Further, cross-linking through the addition of the vinyl-type radicals to various types of unsaturations in polyethylene may also be neglected. Hence we assume that the

cross-linking in acetylenic compounds may take place through the abstraction of a hydrogen atom from a different polymer molecule (Reaction 3) and addition to the resulting polymer radicals (Reaction 4). Since the polymer radicals are always regenerated in these steps, the cross-linking reaction proceed through the chain mechanism. The main-chain scission, which is described as the intramolecular abstraction of a hydrogen (Reaction 5) and the breakdown of the main chain (Reaction 6), is based on the fact that the G(scission) and G(terminal vinyl) increase in acetylene. However, in the case of the derivatives which carries alkyl groups, both G(cross-linking) and G(scission) become smaller than those in vacuum, and G(trans-vinylene) increases. In this case the vinyl-type radicals may be deactivated by the abstraction of a hydrogen from the additives instead of polyethylene (Reaction 7). On the other hand, in the case of fluorine-containing derivatives, Reaction (7) does not occur because of the strong C-F bond, and the effect of these compounds may, therefore, be interpreted in the same way as stated for the case of acetylene.

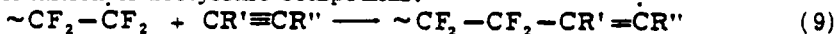
The effect of TFE on these reactions may be interpreted as follows:

### Propagation

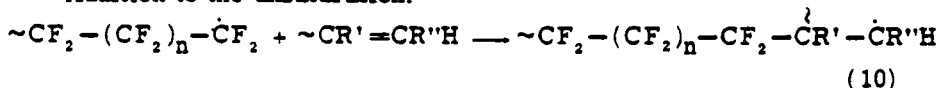
Addition of TFE to the polymer radicals:



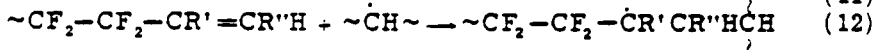
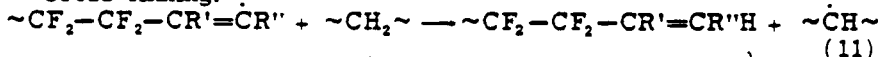
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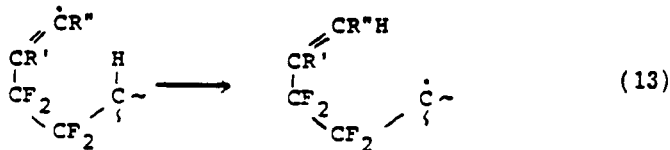
Addition to the unsaturation:

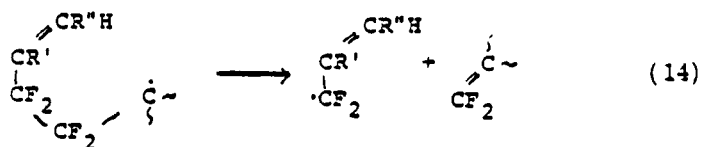


Cross-linking:



Scission:





As stated before, TFE brings a considerable reduction of the main-chain scission. In the above scheme this fact is ascribed to the fact that TFE is inserted between the main chain and vinyl-type radical through Reactions (8) and (9). In this case, even if the intramolecular abstraction of a hydrogen atom (Reaction 13) and the dissociation of C—C bond (Reaction 14) would take place, these reactions could not result in the main-chain scission. Reactions (11) and (12), which lead to the formation of cross-linking, are considered to proceed through the same steps as in the case of Reactions (3) and (4). The increase in G(cross-linking) upon the addition of TFE may be caused by the addition of the propagating radicals with TFE terminal units to the various unsaturations formed in polyethylene (Reaction 10). This is based on the fact that the G(unsaturation) decreases in the presence of TFE.

#### Energetic Consideration on Proposed Reaction Mechanism

Table 4 gives the calculated values of the activation energy of the elementary reactions presented above for the cases in which polyethylene was irradiated in acetylene or in its C<sub>2</sub> to C<sub>3</sub> higher derivatives. The activation energies (E<sub>a</sub>) were estimated by using the semi-empirical equation proposed by Kagiya et al. [13]:

$$E_a = D_i \frac{\{(1 - 2\alpha)D_f + \alpha^2 D_i\}^2}{(D_f - \alpha^2 D_i)^2} \quad (15)$$

where D<sub>i</sub> is the dissociation energies of the bond ruptured and D<sub>f</sub> is that of the bond formed in the reaction. A parameter, α, is related to the heat of the reaction, Q, by the equation α = exp(βQ), and where β is a constant depending on the kind of reaction. For the radical replacement reaction β = 0.0190, and for the addition reaction to the carbon-carbon unsaturated bond β = 0.001554D<sub>i</sub> / (D<sub>f</sub> - 95.0) + 0.03028 is used.

The initiation is the direct interaction between the polymer and

TABLE 4. Estimated Activation Energies of Reactions (2)-(7)

Reaction	Additives	$D_i$ (kcal/mole)	$D_f$ (kcal/mole)	$E_a$ (kcal/mole)
(2)	CH≡CH	59.5	85.7	3.4
	CH≡CCH <sub>3</sub>	58.1	88.6	2.8
	CH≡CC <sub>2</sub> H <sub>5</sub>	57.3	88.8	2.7
	CH≡CC <sub>3</sub> H <sub>7</sub>	58.0	88.8	2.8
	CH <sub>3</sub> C≡CC <sub>2</sub> H <sub>5</sub>	57.3	84.1	3.2
(3)	CH≡CH	94.9	104.2	8.8
	CH≡CCH <sub>3</sub>	94.9	101.1	10.4
	CH≡CC <sub>2</sub> H <sub>5</sub>	94.9	101.1	10.4
	CH≡CC <sub>3</sub> H <sub>7</sub>	94.9	101.1	10.4
	CH <sub>3</sub> C≡CC <sub>2</sub> H <sub>5</sub>	94.9	101.1	10.4
(4)	CH≡CH	57.3	79.7	3.7
	CH≡CCH <sub>3</sub>	56.5	77.1	3.9
	CH≡CC <sub>2</sub> H <sub>5</sub>	56.5	76.6	4.0
	CH≡CC <sub>3</sub> H <sub>7</sub>	56.5	76.6	4.0
	CH <sub>3</sub> C≡CC <sub>2</sub> H <sub>5</sub>	56.0	76.7	3.9
(5)	CH≡CH	94.9	104.0	8.8
	CH≡CCH <sub>3</sub>	94.9	101.1	10.2
	CH≡CC <sub>2</sub> H <sub>5</sub>	94.9	101.1	10.2
	CH≡CC <sub>3</sub> H <sub>7</sub>	94.9	101.1	10.2
	CH <sub>3</sub> C≡CC <sub>2</sub> H <sub>5</sub>	94.9	101.1	10.2
(6)	CH≡CH	66.5	57.3	11.0
	CH≡CCH <sub>3</sub>	66.5	57.3	11.0
	CH≡CC <sub>2</sub> H <sub>5</sub>	66.5	57.3	11.0
	CH≡CC <sub>3</sub> H <sub>7</sub>	66.5	57.3	11.0
	CH <sub>3</sub> C≡CC <sub>2</sub> H <sub>5</sub>	65.5	57.3	10.5
(7)	CH≡CH	103.5	104.2	11.7
	CH≡CCH <sub>3</sub>	82.6	101.1	7.2
	CH≡CC <sub>2</sub> H <sub>5</sub>	74.8	101.1	6.0
	CH≡CC <sub>3</sub> H <sub>7</sub>	74.8	101.1	6.0
	CH <sub>3</sub> C≡CC <sub>2</sub> H <sub>5</sub>	74.8	101.8	5.7

high energy  $\gamma$ -rays. Since a large amount of radiation energy is deposited in the polyethylene molecule by the electronic process, the apparent activation energy of the initial polymer radical formation (1) or (1') can be assumed to be zero.

The cross-linking reaction proceeds through three elementary steps: the addition of acetylenic compounds to the polymer radical (Reaction 2), the abstraction of a hydrogen atom from a neighboring polyethylene to yield a polymer radical and double bond (Reaction 3), and the addition reaction between them to form a cross-link



(Reaction 4). As is shown in Table 4, the activation energy of Reaction (3) is much larger than those of Reactions (2) and (4). Consequently, the ability of the acetylenic compounds to form cross-links is mainly dependent on the occurrence of Reaction (3). Therefore it is reasonable that acetylene, which needs the lowest activation energy for Reaction (3), acts as the most effective cross-linking agent. The retardation by the  $C_2$  to  $C_3$  higher derivatives may be ascribed to the large activation energy of Reaction (3). Another cause for retardation may be the deactivation of the vinyl-type radicals through Reaction (7), which can occur with less activation energy than Reaction (3). The reduction in the weight increment in the presence of the  $C_2$  to  $C_3$  derivatives may also be caused by the occurrence of the degradative chain transfer between the initial polymer radicals and the additives.

In the main-chain scission, Reaction (6) is the rate-determining step. Acetylene gives the lowest activation energy. In the  $C_2$  to  $C_3$  derivatives, Reaction (6) needs a higher activation energy than Reaction (7). Thus, owing to the latter, the vinyl-type radicals are deactivated before entering into Reaction (6), and the main-chain scission decreases in these derivatives. This is consistent with the experimental results.

TABLE 5. Estimated Activation Energies of Reactions (2)-(7)

Reaction	Additives	$D_i$ (kcal/mole)	$D_f$ (kcal/mole)	$E_a$ (kcal/mole)
(2)	$CH\equiv CCF_3$	59.9	88.6	3.2
	$CF_3C\equiv CCF_3$	60.0	84.1	3.6
(3)	$CH\equiv CCF_3$	94.9	101.2	10.4
	$CF_3C\equiv CCF_3$	94.9	101.2	10.4
(4)	$CH\equiv CCF_3$	57.8	78.0	4.1
	$CF_3C\equiv CCF_3$	58.6	76.7	4.5
(5)	$CH\equiv CCF_3$	94.9	101.2	10.2
	$CF_3C\equiv CCF_3$	94.9	101.2	10.2
(6)	$CH\equiv CCF_3$	66.5	57.3	10.5
	$CF_3C\equiv CCF_3$	65.5	57.3	11.5
(7)	$CH\equiv CCF_3$	94.9	101.2	10.2
	$CF_3C\equiv CCF_3$	94.9	101.2	10.2

TABLE 6. Estimated Activation Energies of Reactions (8)-(12)

Reaction	Additives	$D_i$ (kcal/mole)	$D_f$ (kcal/mole)	$E_a$ (kcal/mole)
(8)	$CF_2=CF_2$	39.5	79.6	1.7
(9)	$CH=CH$	59.5	84.6	3.5
	$CH=CCH_3$	58.1	84.6	3.2
	$CH=CC_2H_5$	57.9	84.8	3.2
	$CH=CC_3H_7$	58.0	84.8	3.2
	$CH_2=C=CC_2H_5$	57.3	78.7	3.1
	$CF_3C=CCF_3$	59.9	76.1	4.9
(10)	$CH_2=CHR$	57.3	86.4	2.9
	$CRH=CR'H$	56.5	83.7	3.1
	$CRR'=CR''H$	56.0	74.3	4.3
	$CF_3CH=CHR$	57.3	80.3	3.7
	$CF_3CH=C(CF_3)R$	58.6	81.8	3.7
(11)	$CH=CH$	94.9	104.2	8.9
	$CH=CCH_3$	94.9	101.1	10.5
	$CH=CC_2H_5$	94.9	101.1	10.5
	$CH=CC_3H_7$	94.9	101.1	10.5
	$CH_2=C=CC_2H_5$	94.9	101.8	9.5
	$CF_3C=CCF_3$	94.9	101.8	9.5
(12)	$CH=CH$	58.6	79.7	3.9
	$CH=CCH_3$	57.8	77.1	4.2
	$CH=CC_2H_5$	57.8	76.6	4.3
	$CH=CC_3H_7$	57.8	76.6	4.3
	$CH_2=C=CC_2H_5$	57.3	78.9	3.8
	$CF_3C=CCF_3$	60.0	78.1	4.5

Table 5 gives the activation energies for the case in which the fluorine-containing derivatives are used. Smaller weight increments in PFB may be attributable to the large activation energy of the addition of PFB to the initial polymer radical. The vinyl radicals produced in the reaction with PFB or TFMA have almost the same abilities to abstract a hydrogen from polyethylene. In these cases the degradative chain transfer of the radicals to the substituent groups through Reaction (7) cannot be expected because it needs a large activation energy. Thus, as in the case of acetylene, cross-linking through Reactions (3) and (4), and the main-chain scission through Reactions (5) and (6), may take place.

Table 6 shows the effect of TFE on these reactions. As described before, the  $G(\text{scission})$  decreases by the addition of TFE. This interpretation assumes the insertion of TFE between the polymer and the vinyl radical. The relative probability of the insertion may be

TABLE 7. Estimated Ratio of the Constants,  $k_p/k_t$ 

Additives	CH=CH	CH=CCH <sub>3</sub>	CH=CC <sub>2</sub> H <sub>5</sub>	CH=CC <sub>3</sub> H <sub>7</sub>	CH <sub>3</sub> C=CC <sub>2</sub> H <sub>5</sub>	CF <sub>3</sub> C=CCF <sub>3</sub>
$k_p/k_t$	1.4	1.2	1.2	1.2	1.3	1.4

evaluated by estimating the ratio of the reaction constants,  $k_1/k_2$ . By assuming that the frequency factors of the constants are the same, the ratio was calculated as given in Table 7 from the difference in the activation energies. In all cases the polymer radical adds preferably to TFE rather than to the acetylenic compounds, and acetylene gives the largest ratio. This is consistent with the observation that the G(scission) decreases markedly when TFE is used as mixed with acetylene. PFB also gives a large ratio, but the effect of mixing with TFE is practically negligible. This may be caused by the fact that the G(scission) is substantially small in the atmosphere of this compound.

Table 6 also shows that the TFE radical can add to the terminal vinyl with the lowest activation energy, and that the addition to the tri-substituted unsaturation ( $\text{CRR}'=\text{CHR}''$ ) needs much more activation energy. This is in good agreement with the experimental results that the accelerating effect of TFE on the formation of the cross-linking decreases in the order of acetylene, methylacetylene, butyne-1, pentyne-1, PFB, and pentyne-2.

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