

Acceleration of Fluorine-Containing Monomer—Acetylene System for the γ -Radiation-Induced Cross-Linking of Polyethylene

Hiroshi MITSUI and Fumio HOSOI

Japan Atomic Energy Research Institute, Takasaki Radiation Chemistry Research Establishment, Takasaki, Gunma, Japan.

Tsutomu KAGIYA

Faculty of Engineering, Kyoto University, Kyoto, Japan.

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It has been briefly reported¹ by us that the γ -radiation-induced cross-linking of polyethylene is remarkably accelerated by acetylene, which causes a chain reaction. Recently, we found that the cross-linking with the chain reaction is additionally accelerated by adding some fluorine-containing monomers to acetylene. The purpose of this communication is to report the changes of the gel fraction, weight, and structure of polyethylene irradiated in this system.

High-density polyethylene pellets (Mitsui Petrochemical Industries, Ltd. Hi-zex 2000J) were purified by dissolving in boiling xylene and pouring into a large quantity of cold methanol. The precipitated polyethylene was filtered, washed repeatedly with cold methanol and dried under reduced pressure at room temperature. The purified polyethylene was then hot-pressed into films of about 0.2-mm thickness under a pressure of 200 kg/cm² at 140°C. Fluorine-containing monomers supplied from Daikin Kogyo Co., Ltd. were purified by passing through a 1-m column of silica gel. Commercially available acetylene (99.9% pure) was used, and 1,3-butadiene (Tokyo Kasei Kogyo Co., Ltd.) was purified by distillation before use.

Polyethylene film of about 1.0 g was weighed out into a 50-ml stainless steel cylindrical vessel. After the vessel was repeatedly evacuated and

filled with the mixed gas containing the desired amounts of fluorine-containing monomer and acetylene, the mixed gas was charged into the vessel to an absolute pressure of 3 kg/cm² at 30°C. The vessel was then irradiated by γ -radiation from a ⁶⁰Co source at 30°C. The irradiated film was washed with acetone, evacuated overnight under reduced pressure at room temperature, and weighed. The gel fraction was determined by extracting the sample in a 100-mesh stainless steel basket with boiling xylene for 48 hr. The infrared spectra were measured with a Nippon-Bunko Model DS-301 infrared spectrophotometer using NaCl optics.

As shown in Table I, neither gel formation nor change in polymer weight was observed when the polyethylene was irradiated *in vacuo* to 1.76 Mrad. In the presence of fluorine-containing monomers alone, the gel was not formed, though the polymer weight increased. On the other hand, in acetylene, the gel was formed even by irradiation to 0.66 Mrad, in spite of the slight increase in polymer weight. Both the gel fraction and weight increment were higher when the irradiation was carried out in the mixtures of hexafluoropropene, tetrafluoroethylene, or chlorotrifluoroethylene with acetylene than in acetylene alone. In vinylidene fluoride— and vinyl fluoride—acetylene mixtures, however, the gel fractions

Acceleration of Fluorine-Containing Monomer

Table I. Experimental results of acetylene system^a

Atmosphere	C ₂ H ₂ content, mol%	Dose, Mrad	Weight increment, wt%	Gel fraction, wt%
Vacuum ^b	—	0.66	0.00	0.0
	—	1.76	0.00	0.0
C ₂ H ₂	100.0	0.66	0.07	15.1
	100.0	1.76	0.10	41.5
C ₃ F ₆ —C ₂ H ₂	50.0	1.76	0.80	51.8
	0.0	1.76	1.67	0.0
C ₂ F ₄ —C ₂ H ₂	83.3	0.66	0.26	31.7
	50.0	0.66	0.72	43.9
C ₂ F ₃ Cl—C ₂ H ₂	16.7	0.66	1.09	45.7
	0.0	0.66	1.20	0.0
C ₂ F ₃ Cl—C ₂ H ₂	50.0	1.76	4.25	76.9
	0.0	1.76	15.74	0.0
CH ₂ =CF ₂ —C ₂ H ₂	50.0	0.66	0.13	16.3
	0.0	0.66	0.36	0.0
C ₂ H ₃ F—C ₂ H ₂	50.0	0.66	0.16	14.8
	0.0	0.66	0.99	0.0

^a Reaction conditions: temp, 30°C; total pressure, 3 kg/cm² abs; dose rate, 1.1×10^5 rad/hr.

^b Pressure, 1×10^{-4} mmHg.

were almost equal to the one in acetylene, though the polymer weight somewhat increased.

As shown in the case of the tetrafluoroethylene—acetylene mixture, the accelerating effect varied with the composition of the monomer mixture. In this binary system, therefore, the optimum composition for the cross-linking is considered to depend on the relative reactivity of acetylene and fluorine-containing monomer used. It can be seen from the data listed in Table I that the polymer weight increased by the irradiation in the mixture, and the gel fraction increased in the weight until the maximum gel fraction was attained. The same accelerating effect of tetrafluoroethylene and chlorotrifluoroethylene on

Table II. Experimental results of 1,3-butadiene system^a

Atmosphere	1,3-C ₄ H ₆ constant, mol%	Weight increment, wt%	Gel fraction, wt%
1,3-C ₄ H ₆	100.0	13.5	20.6
C ₂ F ₄ —1,3-C ₄ H ₆	6.6	5.9	67.3
C ₂ F ₃ Cl—1,3-C ₄ H ₆	6.6	13.5	63.3

^a Reaction conditions: temp, 30°C; total pressure, 3 kg/cm² abs; dose rate, 9.6×10^4 rad/hr; total dose, 1.54 Mrad.

1,3-butadiene in the cross-linking was also observed (Table II).

In the infrared spectrum of polyethylene irradiated *in vacuo*, the increase in the absorption peak assigned to the *trans*-vinylene unsaturation (964 cm^{-1}) and the decrease in the peaks due to the terminal vinyl (990 and 908 cm^{-1}) and vinylidene (888 cm^{-1}) groups were observed. When the polyethylene was irradiated in the presence of acetylene, it was observed that the terminal vinyl and *trans*-vinylene unsaturations increased, and the vinylidene group decreased. The results suggest that, by the irradiation in acetylene, the addition of acetylene to polyethylene took place with the dehydrogenation of the polymer. In the spectrum of polyethylene irradiated in 1,3-butadiene, the marked increase in the peaks due to the terminal vinyl and *trans*-vinylene groups, and the non-conjugated double bond (1645 cm^{-1}) was observed, while the peak assigned to the vinylidene group decreased. This result indicates that the grafting of 1,3-butadiene on to polyethylene took place.

As shown in Figure 1, in the infrared spectra

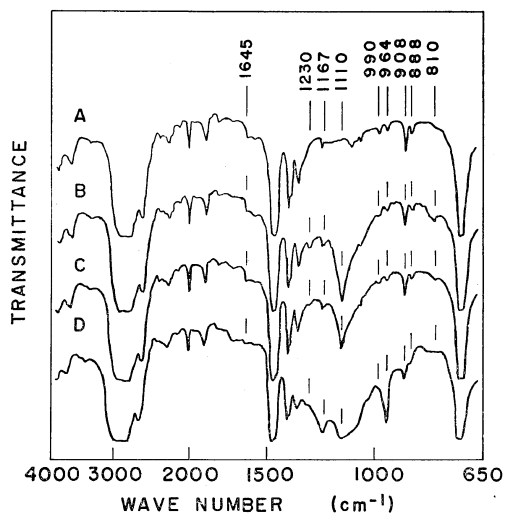


Figure 1. Infrared spectra of polyethylene films unirradiated (A), and irradiated in the presence of tetrafluoroethylene (B) and the mixtures of tetrafluoroethylene with acetylene of 50.0 mol% (C) or 1,3-butadiene of 6.6 mol% (D); temp, 30°C; total pressure, 3 kg/cm² abs; dose rate and total dose, 1.1×10^5 rad/hr and 0.66 Mrad for B and C, 9.6×10^4 rad/hr and 1.54 Mrad for D.

of polyethylene irradiated in the presence of tetrafluoroethylene and the mixtures of this monomer with acetylene or 1,3-butadiene, new absorption bands appeared near 1167 and 1110 cm^{-1} assigned to C—F bond, and near 1230 and 810 cm^{-1} which may be due to C—H bond affected by fluorine. All the peaks assigned to the double bonds decreased by the irradiation in tetrafluoroethylene (Figure 1B). When the polyethylene was irradiated in the mixtures of tetrafluoroethylene with acetylene or 1,3-butadiene, the double bonds increased in comparison with the polyethylene irradiated in tetrafluoroethylene alone (Figures 1C and D), while they decreased as compared with the ones irradiated in acetylene or 1,3-butadiene, respectively. Similar changes in structure were also observed in the other mixtures of fluorine-containing monomer with acetylene or 1,3-butadiene listed in Tables I and II.

From these results, it can be said that fluorine-containing monomers, acetylene, and 1,3-butadiene reacted with polyethylene.

As previously reported,¹ both the cross-linking

and main chain scission of polyethylene are accelerated by acetylene. Hexafluoropropene, tetrafluoroethylene, chlorotrifluoroethylene, and vinylidene fluoride are believed to protect the main chain scission and to promote the incoming reaction of acetylene or 1,3-butadiene by co-grafting on to polyethylene. In the course of the co-grafting, acetylene and 1,3-butadiene may act as polyfunctional monomers to introduce cross-linkage in polyethylene.

A detailed study of the role of fluorine-containing monomers in the marked acceleration of the γ -radiation-induced cross-linking of polyethylene in the presence of acetylene or 1,3-butadiene will be reported on in a subsequent paper.

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