<table>
<thead>
<tr>
<th>Title</th>
<th>Radiation-Induced Crosslinking of Polyethylene in the Presence of Fluorine Containing Monomers</th>
</tr>
</thead>
<tbody>
<tr>
<td>Author(s)</td>
<td>Kagiya, Tsutomu; Yokoyama, Norio</td>
</tr>
<tr>
<td>Citation</td>
<td>Bulletin of the Institute for Chemical Research, Kyoto University (1977), 55(1): 11-19</td>
</tr>
<tr>
<td>Issue Date</td>
<td>1977-03-31</td>
</tr>
<tr>
<td>URL</td>
<td><a href="http://hdl.handle.net/2433/76717">http://hdl.handle.net/2433/76717</a></td>
</tr>
<tr>
<td>Type</td>
<td>Departmental Bulletin Paper</td>
</tr>
<tr>
<td>Textversion</td>
<td>publisher</td>
</tr>
</tbody>
</table>

Kyoto University
Radiation-Induced Crosslinking of Polyethylene in the Presence of Fluorine Containing Monomers

Tsutomu KAGIYA and Norio YOKOYAMA*

Received December 25, 1976

The yield of crosslinking of polyethylene induced by γ-ray irradiation was increased by the presence of fluorine containing monomers such as tetrafluoroethylene and chlorotrifluoroethylene. The gel polymerizations of these monomers were also observed with the increase in the gel fraction. The gel formation in the mixture of chlorotrifluoroethylene and acetylene was higher than that in each monomer alone. The absorption of C-F bond and the decrease in the amounts of unsaturation groups were observed in the IR spectra of the samples irradiated in the presence of fluorine containing monomers. The highest yield of crosslinking was obtained with the use of butadiene grafted polyethylene with the remarkable decrease in the amounts of unsaturation groups. The mechanism of the crosslinking reaction and the role of fluorine containing monomers has been discussed on the basis of these results.

I. INTRODUCTION

Recently, it has been reported that the yield of crosslinking of polyethylene induced by γ-ray irradiation is increased by acetylene and by the mixture of some fluorine containing monomers and acetylene.

The present paper is a report of a more detailed study of the radiation-induced crosslinking of the polyethylene in the presence of fluorine containing monomers. Changes in gel fraction, degree of graft polymerization, chemical structure and mechanical properties of the polyethylene irradiated in the presence of fluorine containing monomers have been measured.

The role of the fluorine containing monomers in the crosslinking reaction has been discussed on the basis of these results.

II. EXPERIMENTAL

Low density (0.92 g/ml) polyethylene film (0.2 mm, thickness, $3.6 \times 10^6$, number average molecular weight) was used in the experiment. Fluorine containing monomers such as tetrafluoroethylene, chlorotrifluoroethylene, hexafluoropropylene, vinylidene fluoride, and vinyl fluoride were supplied from Daikin Kogyo Co. Ltd. γ-Irradiation in the presence of monomers was carried out as follows; polyethylene film (about 0.1 g) was placed in a glass ampule of 40 ml volume. After evacuation, gaseous monomers was introduced to the ampule. The ampule was irradiated with a $^{60}$Co source in the dose rate of 0.05 Mrad/h at room temperature.

The gel fraction was determined by extracting the sample in a 100 mesh stainless steel basket with boiling p-xylene for 20 h. The degree of graft polymerization was

* 鍵谷 勲, 橋山薰夫: Department of Hydrocarbon Chemistry, Kyoto University, Kyoto.
defined as mole of grafted monomer per 100 grams of polyethylene from \((W' - W) \times 100/WM\), where \(W\), \(W'\) are the initial and final weights of the sample, and \(M\) is the molecular weight of monomer. IR spectra of the polyethylene were obtained on a Nippon-Bunko model DS-403G infrared spectrometer. Mechanical properties of the polyethylene were measured with a Shimadzu autograph.

III. RESULTS AND DISCUSSION

1. Crosslinking and Grafting of the Polyethylene Irradiated in Fluorine Containing Monomers

   The gel fraction and the degree of graft polymerization of the samples by \(\gamma\)-ray irradiation of 2.5 Mrad in vacuum and in the presence of various kinds of fluorine containing monomers are listed in Table I. Irradiation in tetrafluoroethylene (TFE) or chlorotrifluoroethylene (CTFE) gave higher yield of crosslinking than that in vacuum. Whereas the gel formation in the presence of hexafluoropropylene (HFP) was nearly equal to that in vacuum. In the presence of vinylidene fluoride (VdF) or vinyl fluoride (VF) brought about lower yield of crosslinking than that in vacuum. The gel fraction and the degree of graft polymerization were increased by the presence of the monomer containing large number of fluorine atom except VdF, and the highest in the presence of CTFE. As shown in Fig. 1, the gel fraction of the polyethylene irradiated in various fluorine containing monomers increased with the degree of graft polymerization. These results indicate the crosslinking in the presence of fluorine containing monomers is one of the side reaction of graft polymerization.

   Figure 2 shows the relation between the irradiation dose and the gel fraction of the polyethylene irradiated in the presence of various fluorine containing monomers. The gel formation was found at the irradiation of 1.25 Mrad in vacuum, and increased with the irradiation dose. The gel fraction of the polyethylene irradiated in the presence of HFP was a little higher than that in vacuum. The gel point was observed at 0.5 Mrad in TFE and the gel fraction was almost same as that in acetylene. The gel fraction of the polyethylene irradiated in CTFE remarkably increased with the irradiation dose without induction period.

<table>
<thead>
<tr>
<th>atmosphere</th>
<th>degree of graft polymerization (mole/100 g)</th>
<th>gel fraction (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>vacuum</td>
<td>—</td>
<td>12.6</td>
</tr>
<tr>
<td>tetrafluoroethylene</td>
<td>0.015</td>
<td>31.8</td>
</tr>
<tr>
<td>chlorotrifluoroethylene</td>
<td>0.116</td>
<td>62.0</td>
</tr>
<tr>
<td>hexafluoropropylene</td>
<td>0.009</td>
<td>12.8</td>
</tr>
<tr>
<td>vinylidene fluoride</td>
<td>0.003</td>
<td>5.8</td>
</tr>
<tr>
<td>vinyl fluoride</td>
<td>0.013</td>
<td>7.3</td>
</tr>
</tbody>
</table>
Radiation-Induced Crosslinking of Polyethylene

Fig. 1. Gel fraction and number of terminal vinyl of polyethylene versus degree of graft polymerization.

Fig. 2. Relation between irradiation dose and gel fraction of polyethylene irradiated in the presence of fluorine containing monomers.

O; vacuum,  O; tetrafluoroethylene,  O; chlorotrifluoroethylene,  O; hexafluoropropylene,  ●; acetylene.
The Charlesby Pinner’s plot\textsuperscript{43} did not give a straight line in the experiment irradiated below 5.0 Mrad. It might be caused by low degree of crosslinking in this experiment. While, in the presence of CTFE, the results give a straight line, and the G values for chain scission and crosslinking were obtained as 6.9 and 7.6 respectively.

2. IR Spectra of the Polyethylene

Changes in IR spectra of the polyethylene irradiated in the presence of fluorine containing monomers are shown in Fig. 3 and Table II. The various kinds of absorption bands assigned to C-F bonds were observed in the range from 1400 cm\textsuperscript{-1} to 1100 cm\textsuperscript{-1}. The bands assigned to C-F bonds at 1230, 1175, and 1100 (strongest) cm\textsuperscript{-1} were observed in the polyethylene irradiated in the presence of TFE. In the polyethylene irradiated in the presence of CTFE, the bands appeared at 1300, 1258, and 1072 (strongest) cm\textsuperscript{-1}. These C-F bonds increased with the irradiation dose.

On the other hand, the band at 964 cm\textsuperscript{-1} assigned to trans vinylene increased under the irradiation in vacuum, whereas the band at 908 cm\textsuperscript{-1} assigned to terminal vinyl slightly decreased. In the presence of fluorine containing monomers, especially CTFE, the remarkable decrease in the terminal vinyl was observed under the irradiation. The gel fraction of the polyethylene irradiated in fluorine containing monomers increased with the decrease in the terminal vinyl as shown in Fig. 1. The terminal vinyl decreased remarkably with the degree of graft polymerization.

These results indicate that, in the presence of fluorine containing monomers, side chain polymer radical formed by grafting of fluorine containing monomers (M)
Radiation-Induced Crosslinking of Polyethylene

Table II. Changes in IR Spectra of the Polyethylene Irradiated in the Presence of Fluorine and Unsaturated Monomers

<table>
<thead>
<tr>
<th>atmosphere</th>
<th>dose</th>
<th>C-F*</th>
<th>trans vinylene**</th>
<th>terminal vinyl**</th>
<th>vinyldiene**</th>
</tr>
</thead>
<tbody>
<tr>
<td>non-irrad.</td>
<td>0.0</td>
<td>—</td>
<td>0.046</td>
<td>0.097</td>
<td>0.271</td>
</tr>
<tr>
<td>vacuum</td>
<td>5.0</td>
<td>—</td>
<td>0.122</td>
<td>0.091</td>
<td>0.271</td>
</tr>
<tr>
<td>acetylene</td>
<td>1.0</td>
<td>—</td>
<td>0.091</td>
<td>0.108</td>
<td>0.265</td>
</tr>
<tr>
<td></td>
<td>2.5</td>
<td>—</td>
<td>0.110</td>
<td>0.135</td>
<td>0.265</td>
</tr>
<tr>
<td>tetrafluoroethylene</td>
<td>1.0</td>
<td>0.56</td>
<td>0.046</td>
<td>0.075</td>
<td>0.227</td>
</tr>
<tr>
<td></td>
<td>2.5</td>
<td>0.96</td>
<td>0.038</td>
<td>0.027</td>
<td>0.145</td>
</tr>
<tr>
<td></td>
<td>5.0</td>
<td>1.30</td>
<td>0.030</td>
<td>0.022</td>
<td>0.101</td>
</tr>
<tr>
<td>chlorotrifluoroethylene</td>
<td>1.0</td>
<td>0.44</td>
<td>0.030</td>
<td>0.022</td>
<td>0.044</td>
</tr>
<tr>
<td></td>
<td>2.5</td>
<td>1.16</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td></td>
<td>5.0</td>
<td>1.39</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>hexafluoropropylene</td>
<td>1.0</td>
<td>0.27</td>
<td>0.061</td>
<td>0.086</td>
<td>0.233</td>
</tr>
<tr>
<td></td>
<td>2.5</td>
<td>0.37</td>
<td>0.068</td>
<td>0.070</td>
<td>0.227</td>
</tr>
</tbody>
</table>

*, log Io/I. **, number/1000 C.

reacts with the terminal vinyl contained in polyethylene to lead crosslinking without consuming the number of radical.

\[
\begin{align*}
\sim \text{CH}_2\text{CH}^- & \underbrace{\text{(M)}_n} + \sim \text{CH}_2\text{CH}\sim + \sim \text{CH}_2\text{CH}-\text{CH}_2\sim \rightarrow \sim \text{CH}_2\text{CH}\sim \\
& + \sim \text{CH}_2\text{CH}-\text{CH}_2\sim \rightarrow \sim \text{CH}_2\text{CH}\sim
\end{align*}
\]

\[
\begin{align*}
\sim \text{CH}_2\text{CH}\sim & \rightarrow \sim \text{CH}_2\text{CH}\sim \\
& + (m+1)\text{M} \rightarrow \sim \text{CH}_2\text{CH}\sim
\end{align*}
\]

3. Crosslinking of the Polyethylene Irradiated in the Mixture of CTFE and Acetylene

As has already been reported by us,\textsuperscript{4}) radiation-induced crosslinking of polyethylene is promoted by the presence of the mixture of unsaturated monomers and
fluorine containing monomers. In Fig. 4 is shown the relation between the molar ratio of the mixture (CTFE-acetylene) and the degree of polymerization, and the gel fraction of the samples. The degree of graft polymerization of the samples remarkably increased by the addition of CTFE to acetylene. The gel formation in the mixture was higher than that in acetylene and CTFE alone. The highest gel fraction was obtained in the equi-molar mixture of CTFE and acetylene.

It can be considered from Fig. 4 that the polymer vinyl radical formed by the addition of acetylene makes crosslinking due to hydrogen abstraction mechanism:

\[
\sim \text{CH}_2\sim \cdot \text{CH} + \text{CH}≡\text{CH} \rightarrow \sim \text{CH}_2\sim \text{CH} \sim
\]

\[
\sim \text{CH}_2\sim \cdot \text{CH} + \sim \text{CH}_2\sim \text{CH} \rightarrow \sim \text{CH}_2\sim \text{CH} \sim
\]

In the presence of acetylene containing a small amounts of CTFE, graft reaction of CTFE to the polymer vinyl radical results in the formation of internal vinylene group as functional group in side chain.
Radiation-Induced Crosslinking of Polyethylene

On the contrary, in the presence of CTFE containing a small amount of acetylene, CTFE grafts to chain side radical, and acetylene reacts with the radical to form polymer vinyl radical. The radical makes crosslinking due to hydrogen abstraction mechanism.

\[
\begin{align*}
\sim \text{CH}_2\text{CH} \sim + n \text{CF}_2=\text{CFCI} & \rightarrow \sim \text{CH}_2\text{CH} \sim \\
\text{(CF}_2\text{CFCI)}_{n-1}\text{CF}_2\cdot \text{CFCI} & \rightarrow \sim \text{CH}_2\text{CH} \sim \\
\sim \text{CH}_2\text{CH} \sim + \text{CH}_3\equiv \text{CH} & \rightarrow \sim \text{CH}_2\text{CH} \sim \\
\text{(CF}_2\text{CFCI)}_{n-1}\text{CH} = \cdot \text{CH} & \rightarrow \\
\sim \text{CH}_2\text{CH} \sim & \rightarrow \\
\text{(CF}_2\text{CFCI)}_{n-1}\text{CH}_2\text{CH} & \rightarrow \\
\sim \text{CH}_2\text{CH} \sim & \rightarrow \\
\text{(CF}_2\text{CFCI)}_{n-1}\text{CH}_2\text{CH} & \rightarrow \\
\end{align*}
\]

Internal vinylene group may also be formed by the graft reaction of CTFE to side chain polymer radical in graft branch.

\[
\begin{align*}
\sim \text{CH}_2\text{CH} \sim + \text{CF}_2=\text{CFCI} & \rightarrow \\
\text{(CF}_2\text{CFCI)}_{n-1}\text{CH} = \cdot \text{CH} & \rightarrow \\
\sim \text{CH}_2\text{CH} \sim + \text{CF}_2=\text{CFCI} & \rightarrow \\
\text{(CF}_2\text{CFCI)}_{n-1}\text{CH} = \cdot \text{CH} & \rightarrow \\
\end{align*}
\]

4. Crosslinking of the Butadiene Grafted Polyethylene Irradiated in the Presence of Fluorine Containing Monomers

In order to give an unsaturation groups to the sample, polyethylene was irradiated with 2.5 Mrad in the presence of butadiene at normal pressure. The absorption of unsaturation groups in the IR spectra and the weight increase of sample were observed without gel formation. The butadiene grafted polyethylene was irradiated in the presence of fluorine containing monomers. Table III indicates that the extent of unsaturation groups decreased remarkably under the irradiation in the presence of fluorine containing monomers, especially CTFE. The gel fraction increased with the decrease in the amounts of the terminal groups. In the presence of CTFE, the gel fraction of the butadiene grafted polyethylene (79 %) was higher than that (62 %) of the non-grafted polyethylene with the same dose of irradiation.

On the basis of these results, a following crosslinking mechanism of the polyethylene in the presence of fluorine containing monomers might be proposed. Two radicals formed under the irradiation in vacuum may lead to crosslinking as a result of radical recombination. In the presence of fluorine containing monomers,
Table III. Gel Fraction and Changes in IR Spectra of the Butadiene Grafted Polyethylene Irradiated with 2.5 Mrad in the Presence of Fluorine Containing Monomers

<table>
<thead>
<tr>
<th>atmosphere</th>
<th>gel fraction (%)</th>
<th>degree of graft polymerization (mole/100 g)</th>
<th>trans vinylene number /1000 C conversion(%)</th>
<th>terminal vinyl number /1000 C conversion(%)</th>
<th>vinylidene number /1000 C conversion(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>control</td>
<td>0.0</td>
<td>0.100</td>
<td>8.64</td>
<td>3.10</td>
<td>0.42</td>
</tr>
<tr>
<td>vacuum</td>
<td>38.9</td>
<td>—</td>
<td>7.91</td>
<td>8.6</td>
<td>2.60</td>
</tr>
<tr>
<td>tetrafluoroethylene</td>
<td>32.8(57.4)</td>
<td>0.002</td>
<td>7.28</td>
<td>15.8</td>
<td>2.32</td>
</tr>
<tr>
<td>chlorotrifluoroethylene</td>
<td>79.0(62.0)</td>
<td>0.102</td>
<td>2.80</td>
<td>67.6</td>
<td>0.15</td>
</tr>
</tbody>
</table>

( ) ; the gel fraction of non-grafted polyethylene irradiated with 5.0 Mrad

side chain polymer radical formed by grafting of CTFE reacts with the unsaturation groups to take place crosslinking as described in the reaction (1) and (2).

As described before, the degree of crosslinking increased with the increase in the degree of graft polymerization. The order of the reactivity of fluorine containing monomers in the graft polymerization was CTFE > TFE > VF > HFP > VdF. The degree of graft polymerization is dependent on the reactivity of the monomer in the graft polymerization. Therefore, with the use of the polyethylene containing the same amounts of terminal vinyl groups, the acceleration effect of fluorine con-

Fig. 5. Relation between gel fraction and mechanical properties of polyethylene irradiated with 5.0 Mrad in the presence of fluorine containing monomers.
Radiation-Induced Crosslinking of Polyethylene

taining monomer in the crosslinking increased with the increase in the monomer reactivity in the graft polymerization.

5. Mechanical Properties of the Crosslinked Polyethylene

Figure 5 shows the mechanical properties of the polyethylene in the presence of fluorine containing monomers. The increase of yield ($\sigma_y$) and break point ($\sigma_b$), and the decrease of elongation were observed after the irradiation in the presence of fluorine containing monomers. The yield and break point increased slightly with the gel fraction, whereas the elongation decreased remarkably with high degree of gel (over 50%).

ACKNOWLEDGMENT

The authors thank Professor J.F. Rabek, the Royal Institute of Technology, Stockholm, Sweden for many helpful discussions and suggestions, and the Institute for Chemical Research, Kyoto University for permitting us to use the $^{60}$Co $\gamma$-ray irradiation apparatus.

REFERENCES