Temperature Dependence of Radiation Effects in Polyethylene

G. Wu,[1] Y. Katsumura,[1]* H. Kudoh,[2] Y. Morita[2] and T. Seguchi[2]

[1]Nuclear Engineering Research Laboratory, School of Engineering,

The University of Tokyo, Shirane 2-22, Shirakata, Naka-gun, Ibaraki 319-1106, Japan

[2]JAERI-Takasaki, Watanuki 1233, Gunma 370-12, Japan

Temperature dependence of crosslinking and gas evolution under γ-irradiation was studied for high-density and low-density polyethylene samples in the 30-360 °C range. It was found that crosslinking was the predominant process up to 300 °C and the gel point decreased with increasing temperature. At above 300 °C, however, the gel fraction at a given dose decreased rapidly with temperature and the action of radiation turned to enhance polyethylene degradation. Yields of H_2 and hydrocarbon gases increased with temperature and the compositions of hydrocarbons were dose dependent.

Introduction

Radiation-induced cross-linking has been proved to be an effective method for improving the material properties of polyethylene and numerous papers[1,2] have been published. Many factors such as molecular weight, crystallinity, temperature, irradiation atmosphere, affect the cross-linking efficiency. In the past, irradiation of polyethylene was studied from –269 °C to around 130°C (m.p. of PE) and the temperature effect on crosslinking efficiency, gas evolution, tensile property, etc. was evaluated. Irradiation in the melt has some advantages such as the decreased gel point, increased network tightness and production of a homogeneous network. Here we made an effort to investigate the temperature effect on cross-linking efficiency and gas evolution over a very wide temperature range.

Experimental

High-density polyethylene (HDPE) and low-density polyethylene (LDPE) samples free of additives were used as received. The molecular weights were M_n 2×10^4 /M_w 9×10^4 for LDPE and M_n 9×10^3 /M_w 1.6×10^5 for HDPE. Isobutyl branches exist along the polymer chains of HDPE since trivial amounts of 4-methyl 1-pentene were added in the polymerization. Samples of 3-10 g of polyethylene were put into the Pyrex glass ampules (ca. 50 ml) and the ampules were sealed after evacuation. The prepared

samples were irradiated with γ-rays at a dose rate of 3.5 kGy/h at 30-220 °C for HDPE and at 30-360 °C for LDPE.

After irradiation, the evolved gas was separated and its compositions were analyzed by gas chromatograph technique. The gel fraction was determined after removing the soluble portion by immersing the irradiated sample into boiling xylene for two 6-h intervals, each in the fresh solvent.

Results and Discussion

Temperature dependence of crosslinking

Figure 1a shows the gel fraction as a function of dose for LDPE at 30-300 °C. It can be seen that the crosslinking efficiency is enhanced with temperature and the temperature is especially pronounced in the low-dose region. At high doses, the influence of temperature is insignificant. Figure 1b further shows the gel fraction at temperatures of 30-360 °C after 20 kGy for LDPE. It is more clearly to see the temperature effect on crosslinking and, in addition, the rapid decrease of crosslinking efficiency above 300 °C. No gel was determined at 360 °C. This indicates that radicals formed by radiolysis undergo decomposition rather than cross-linking. The analysis of molecular weight distribution for LDPE samples irradiated at 360 °C revealed that radiation enhanced polymer degradation when compared with

purely heated samples, which is in agreement with our previous work[3] on high temperature irradiation of n-hexadecane.
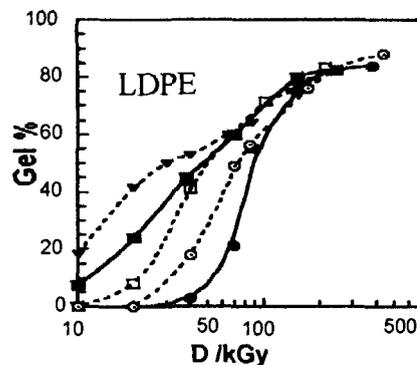

Fig. 1a Correlation of gel fraction with dose for LDPE at 30 (●), 100 (○), 150 (□), 220 (■), 300 (▼) °C.
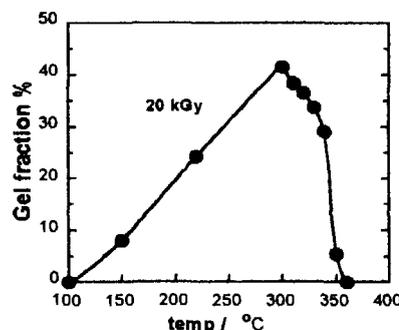

Fig. 1b Variation of gel fraction with irradiation temperature for LDPE.

Raising temperature also favors the crosslinking of HDPE. However, owing to its relative higher molecular weight, the temperature dependence of crosslinking efficiency was not so significant as that for LDPE.

G(x) and G(s)

G values of crosslinking and scission, G(x) and G(s), were estimated for discussion of the temperature. We use the Charlesby-Rosiak formula[4], which always allows one to plot the sol/dose relation in the form of straight line, to analyze the sol/dose data.

$$s + s^{1/2} = 0.5\lambda + 0.5(4 - \lambda)$$

$$\times (D_v + D_g)/(D_v + D) \quad (1)$$

where s is the sol fraction, λ is the ratio $G(s)/G(x)$, D_g is gel point, D_v is the virtual dose, and D is the absorbed dose. The definition of D_v is a dose required for changing the MWD of the polymer under study in such a way that M_w/M_n would be equal to 2. Formula (1) seems more suitable for polymer with low degree of crystallinity or in the amorphous state. Fitting of the data with eq.(1) using the experimentally obtained s, D and D_g enables one to get λ and D_v. Then values of $G(x)$ were calculated from λ. Table 1 present such parameters for LDPE and HDPE at varying temperatures

Table 1. Parameters at Different Temperatures for LDPE and HDPE

	T /°C	D_g/kGy	D_v/kGy	λ	$G(x)$[a]	$G(x)$ at λ=0
LDPE	30	42	24 ± 17	0.44 ± 0.21	1.4	1.3
	100	27	26 ± 4	0.48 ± 0.10	2.3	2.1
	150	16	25 ± 4	0.50 ± 0.08	3.7	3.3
	220	8.5	35 ± 5	0.56 ± 0.11	7.2	6.2
	300	5.6	8 ± 1	1.61 ± 0.06	15.9	–
HDPE	30	16	42 ± 14	1.46 ± 0.21	2.8	1.8
	100	13	48 ± 10	1.32 ± 0.18	3.5	2.4
	150	9.0	48 ± 8	1.18 ± 0.14	4.6	3.3
	220	6.5	38 ± 6	1.32 ± 0.13	6.7	4.5

[a]Calculated by $G(x) = 1.92 \times 10^7/[M_w D_g(4-\lambda)]$, D_g in kGy.

As can be seen, D_g decreases and $G(x)$ increases with temperature. Because λ is nearly independent of temperature up to 220 °C, $G(s)$ also increases with temperature. The large λ value at 300 °C that at other temperatures for LDPE is indicative the considerable degradation process. It is also noted that the λ for HDPE is higher than for LDPE by a factor of 2-3. This is probably due to wider molecular weight distribution of HDPE. In the gel fraction determination, low-molecular-weight fraction is determined in practice as the "sol".

Gas Evolution

At 30-220 °C, the evolved gas comprises mostly H_2 and the H_2 fraction is always higher than 90 vol% despite its slightly decrease with temperature. However, the H_2

fraction at 300 °C for LDPE decreased to 60-80 vol%, due to production of a considerable yield of hydrocarbon gases. We found that G values of H_2 increased slightly with temperature and decreased with dose at a given temperature.
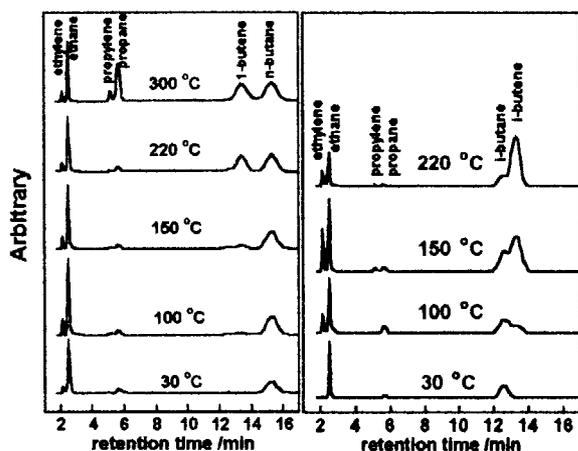

Fig.2 Chromatograms of evolved hydrocarbons from LDPE (left) and HDPE (right) at various temperatures.

A number of gases such as methane, ethane, butane, etc. were also detected in the evolved gas. These gases are formed as the result of scission of branching groups. Figure 2 shows chromatograms of the C_2-C_4 hydrocarbons for LDPE and HDPE. It is noted that both saturated and unsaturated hydrocarbons are evolved. Of particular interest is the formation of iso-butane and iso-butene from HDPE compared to n-butane and 1-butene from LDPE. This is due to the existence of iso-butyl branching in HDPE. The relative fraction of alkene gases is increasing with

temperature and decreasing with dose at the same temperature. The latter implies the addition of alkene to macroradicals. The total yield of hydrocarbon gas increases with temperature since raising the temperature favors the scission of branching.

Conclusion

For Both LDPE and HDPE, higher temperature of irradiation leads to the increase of crosslinking efficiency and gas yield. The temperature dependence of crosslinking could be attributed the addition of radicals to the vinyl end groups and vinylenes present in the polymer. The scission process is not significant below 220 °C but becomes important above 300 °C.

Reference

1. M. Dole. The Radiation Chemistry of Macromolecules; Academic Press: New York and London, 1973; Vols I and II.

2. B. J. Lyons *J. Radiat. Phys. Chem.*, 1993, 42, 197.

3. G. Wu, Y. Katsumura, C. Matsuura, K. Ishigure, J. Kubo, *Ind. Eng. Chem. Res.*, 1997, 36, 1978; 1997, 36, 3498.

4. J. Olejniczak, J. Rosiak, A. Charlesby, *Radiat. Phys. Chem.*, 1991, 37, 499.