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Radiation-induced reactions of syndiotactic polypropylene

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Summary

The radiation-induced reaction of highly syndiotactic polypropylene was examined by following the changes in limiting viscosity, molecular weight distribution, and stereoregularity. The degree of syndiotacticity clearly decreased even when there was no apparent change in molecular weight. Irradiation at an elevated temperature caused a marked decrease in molecular weight and formation of unsaturated residues.

Introduction

It is well known that the main reactions of polypropylene under γ-ray irradiation at a low dose rate and at a high dose rate are decomposition and crosslinking, respectively [1].

In recent years, isotactic [2], syndiotactic [3] and atactic [4] polypropylenes having a narrow molecular weight distribution have been prepared using homogeneous catalysts. Ewen [3] was the first to succeed in the polymerization of highly syndiotactic polypropylene. In the present work we examined the reaction mechanism of the change in the molecular weight of highly syndiotactic polypropylene by γ-ray irradiation.

Experimental

Propylene of HL-grade from Osaka Petrochemical Industries (Japan) was used without further purification. 1-Methyl-1-ethyliden(cyclopentadienyl-1'-fluorenyl)zirconium dichloride was prepared as described in the literature [3]. Methylaluminoxane was purchased from Tosoh Akzo Co.. Propylene (3 kg/cm^2) was polymerized in an autoclave (2 l) at 293 K by using the catalyst 1-methyl-1-ethyliden-(cyclopentadienyl-1'-fluorenyl)zirconium dichloride (2 mg/l) and methylaluminoxane (680 mg/l) in toluene (1 l). The obtained polymer was highly syndiotactic (see No. 1 in Table 2). Limiting viscosity ([η]) was measured at 408 K in tetrahydronaphthalene solution. The molecular weight distribution of polymers was determined at 408 K with Waters Associates ALC/GPC (model 150C) equipped with a Shodex AD80MS column by using 1,2,4-trichlorobenzene as the solvent. GPC

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was calibrated by using standard polystyrene. ^{13}C-NMR spectra were obtained with JEOL GX270 operated in the FT mode. NMR samples were prepared by dissolving polymers (200 mg) in 1,2,4-trichlorobenzene (2.5 ml) and benzene-d_6 (0.5 ml).

Samples for irradiation were prepared as follows. The glass tube containing syndiotactic polypropylene powder was connected to a vacuum line, evacuated to less than 10^{-4} mmHg, then heated up to 473 K for 1 hour, and finally the glass tube was cooled and sealed in vacuo. A quenched sheet was obtained by melting the polymer at 503 K, pressing the melt between two steel plates and then dropping in a dry ice-methanol bath. The sheet was introduced in a glass tube and sealed in vacuo (less than 10^{-4} mmHg). γ-Ray irradiation was carried out with the ^{60}Co source of the Research Reactor Institute of Kyoto University under the condition of 88 to 93 KGy/h at 298. 363 and 473 K. To remove the remaining radicals after γ-ray irradiation the polymers were treated with methanol in a nitrogen atmosphere for at least 24 h, or heated up to 373 K for 1 h in vacuo.

Results and Discussion

Table 1 shows the data of [η], Mv, and the molecular weight distributions (MW/MN) measured by GPC. The Mv was calculated by using the equation $[\eta] = 8.0 \times 10^{-5} \times Mv^{0.80}$. γ-Ray irradiation did not reduce [η] at 298 K, but decreased it at 363 K and 473 K. The number of main chain scission points per 100 propylene units **n** was calculated as follows.

$$\mathbf{n} = 100 \times (N_0 - N_i)/NN = 4200 \times (1/Mn_0 - 1/Mn_i) \qquad (1)$$

$$Mn_i = 42 \times (NN/N_i) \qquad (2)$$

$$Mn_0 = 42 \times (NN/N_0) \qquad (3)$$

where NN is the number of propylene units in the system, N_i and N_0 are the number of molecules in the system before and after irradiation, respectively; Mn_i and Mn_0 are the number

Table 1
Radiation-induced reaction of syndiotactic polypropylene

Sample No.	Radiation temp./K	Dose /Mrad	After-treatment	[η]	Mv /10^5	MW/MN
1	-	0	MeOH	1.40	2.01	2.1
2	298	3	MeOH	1.41	2.03	2.7
3	363	3	MeOH	1.25	1.75	2.4
4	473	3	MeOH	0.40	0.42	1.7
5[a]	298	6	MeOH	1.45	2.10	3.6
6[a]	298	6	Heating	1.83	2.81	4.3

[a] For the quenched sheet.

Table 2
Pentad fraction ratio of the samples

Sample No.	Pentad fraction rrrr	rmmr	rrmm	rmrr	rmrm	rrrm
1	0.932	0.011	0.020	0.010	0.001	0.026
2	0.913	0.014	0.029	0.011	0.001	0.032
3	0.913	0.014	0.028	0.010	0.001	0.034
4	0.898	0.017	0.034	0.012	0.001	0.038
5[a]	0.909	0.014	0.030	0.010	0.001	0.036
6[a]	0.908	0.013	0.031	0.010	0.001	0.036

a) For the quenched sheet.

average molecular weight before and after irradiation, respectively. In this case Mn was calculated by the equation Mn = (Mv)/(MW/MN), since the error of MN measured by GPC was larger than that of Mn calculated by the equation shown above. The number of main chain scission points per 100 propylene units was 0.013 at 298 K, 0.014 at 363 K and 0.13 at 473 K. The G-value was 1.0 at 298 K, 1.1 at 363 K, and 9.6 at 473 K.

The NMR spectra of the samples irradiated at 298 K (No. 2) and 363 K (No. 3) showed no new peaks. However, for the sample irradiated at 473 K (No. 4), at least 6 new peaks were observed at 14.5, 22.5, 30.5, 46.2, 111.5 and 144.5 ppm. No. 5 and 6 in Table 1 show the results for the quenched sheet. Though no new peak was found in the NMR spectra for the quenched sheet, an increase in molecular weight was observed. The increase of [η] was about 31 % for No. 6 after heat treatment. For the quenched sheet, crosslinking may occur in the amorphous region although the probability of crosslinking is rather small.

Table 2 shows the pentad fractions of the irradiated polymer calculated by the NMR peak intensity of methyl carbon of propylene units. The assignment of peaks was made according to Asakura [5]. Pentad fractions of rmmr, rrmm and rrrm increased by γ-ray irradiation. This phenomenon is explained by the increase of mm triad. As shown in Scheme (a) the radical produced by removing the H or methyl radical takes a planar conformation of sp^2-hybrid orbital, and then it couples with the H or methyl radical. By this reaction the rrrr pentad changes to rmmr pentad. The increase of the mm triad increases the rmmr, rrmm and rrrm pentad. As the coupling occurs in two directions, two times of the probability of producing the mm triad is the probability of a C-H or $C\text{-}CH_3$ scission. So the probability of the scission and coupling, i.e., the increase of mm triad Fmm can be calculated as follows.

$$Fmm = (Frmmr + Frrmm + Frrrm)/5 \qquad (4)$$

where Frmmr, Frrmm, and Frrrm are the increase of pentad

Scheme

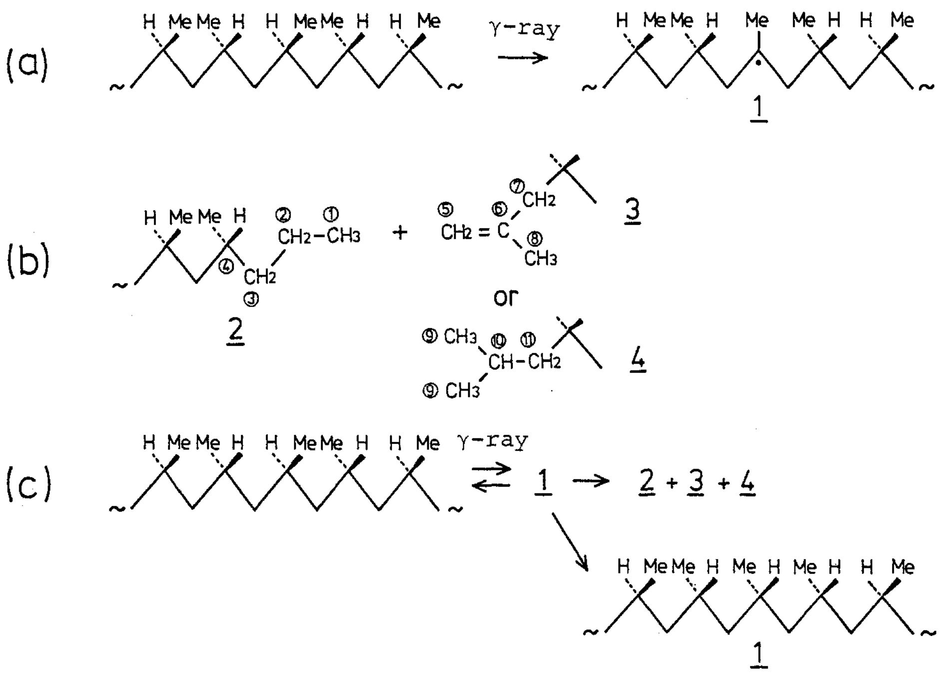

Table 3
Chemical shift (ppm) of ^{13}C NMR for the carbons of the products

	No. of carbon[a]										
	1	2	3	4	5	6	7	8	9	10	11
Calc.	14.4	20.0	39.6	30.5	111.3	143.6	44.2	23.9	22.6	25.9	46.5
Obs.	14.5	-	-	30.5	111.5	144.5	-	-	22.5	-	46.2

[a] No.'s of carbon correspond to those of the reaction products indicated in Scheme (b).

fractions of rmmr, rrmm, and rrrm, respectively. A two-fold of the increase of mm triad (Fmm) means the probability of C-H or $C-CH_3$ scission, so the side chain scissions per 100 propylene units were 0.72, 0.76 and 1.28 for samples No. 2, No. 3 and No. 4, respectively, and the G-values were 55, 58, and 98, respectively. Although the decrease in molecular weight was very small for No. 2, the reaction of side chain scission occurred considerably. In the case of No. 4, new peak signals of ^{13}C-NMR were observed and compared with the chemical shifts calculated by the method of Lindeman [6]. Irradiation products shown in Scheme (b) were assumed and their peak signals were assigned as shown in Table 3. Scheme (c) shows the proposed reaction path under γ-ray irradiation for syndiotactic polypropylene. The detailed reaction mechanism of the molecular weight increase is still unknown, but we tentatively propose that the molecular weight increase by heating after γ-ray irradiation is induced by the addition of radical **1** to the double bond **3**.

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