

# Effect of Radiation on the Crosslinking and Branching of Polypropylene

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**ABSTRACT:** To make crosslinked polypropylene (PP) and PP with high melting strengths, we studied the effects of radiation on the crosslinking and branching of PP in detail with the Charlesby–Pinner (C–P) equation. We studied the radiation crosslinking and branching behavior of homopolypropylene (HPP), impact copolypropylene (IPP), and random copolypropylene (RPP) and used the C–P equation for some parameter calculations. We found that (1) the C–P equation seemed applicable when PP with a multifunctional crosslinking agent was irradiated within a certain dose range in air and (2) IPP had the highest gel dose value, crosslinking  $G$  value/scission  $G$  value, and gel fraction after irradiation among HPP, RPP, and IPP; therefore, IPP is the best material for making radiation crosslinking and radiation branching PP among HPP, RPP, and IPP. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 85: 1758–1764, 2002

**Key words:** radiation; crosslinking; branched; poly(propylene) (PP)

## INTRODUCTION

Crosslinking and branching can improve some properties of polypropylene (PP); therefore, many researchers have studied these fields.<sup>1–4</sup> Radiation is the second best method for making crosslinking PP after the silane–water crosslinking method.<sup>5</sup> Branching can increase the melting strength of PP, and radiation is the best method to make branched PP. All three kinds of PP [i.e., homopolypropylene (HPP), random copolypropylene (RPP), and impact copolypropylene (IPP)] can be used to make crosslinked PP and branched PP with the irradiation method. For making crosslinked PP, a PP resin with better radiation

stability and higher gel fraction after irradiation is expected; for making branched PP, the PP resin with better radiation stability and larger gel dose ( $R_g$ ) is preferred. The parameters related to radiation stability and  $R_g$  can be obtained with the Charlesby–Pinner<sup>6</sup> (C–P) equation:

$$S^{1/2} + S = P_0/q_0 + (q_0\mu R)^{-1} \quad (1)$$

where  $S$  is the soluble fraction.  $P_0$  is a constant representing the susceptibility of a polymer system to fracturing;  $P_0$  is the proportion of main chain units fractured per unit of absorbed dose ( $R$ ).  $q_0$  is a constant representing the susceptibility of a polymer system to crosslinking;  $q_0$  is the proportion of monomer units crosslinked per unit of  $R$ .  $\mu$  is the initial number-average degree of polymerization. This equation was deduced based on five hypotheses, including

- Initial molecular weight distribution is of the random type.

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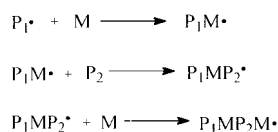
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**Table I Mechanical Properties of PP and Branched PP**

	Tensile Strength (MPa)	Izod Impact Strength (Notched; J/m)	Flexural Strength (MPa)	Flexural Modulus (GPa)	Heat Distortion Temperature (°C)
PP-1	37.9	40.9	38.1	1.69	118
Branched PP-1	39.4	42.6	40.6	1.73	123

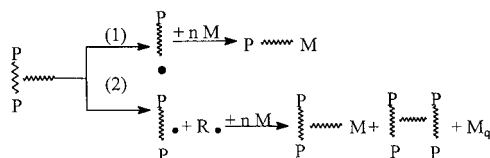
- Crosslinking and degradation occur at random and consecutively.
- Crosslinking and degradation are proportional to the radiation dose.
- The disturbing effect of the end groups can be ignored.
- The intramolecular crosslinking can be ignored.

Charlesby's reaction model for radiation crosslinking of a polymer with a crosslinking agent<sup>7</sup> is as follows:



It seems that radiation crosslinking of a polymer with a multifunctional monomer is not a random reaction according to the previous model; therefore, the C-P equation is not applicable in the radiation crosslinking of a polymer with a multifunctional monomer. However, it has been found that  $S^{1/2} + S$  and  $R^{-1}$  have a very good linear relationship according to our experimental results of the radiation crosslinking of PP, which is shown in this article. It seems that the C-P equation is applicable in the radiation crosslinking of PP with a multifunctional monomer in a certain dose range in air. The possible reason for that is given next.

During the course of the radiation crosslinking of PP with a multifunctional monomer, there exist two types of reaction, shown as follows:<sup>8</sup>



If the polymer prefers to degrade, Reaction 1 is dominant. If the polymer prefers to crosslink, Re-

action 2 is dominant, ( $R \cdot$  is  $H \cdot$  or  $CH_3 \cdot$  in this reaction). The product in Reaction 2 is composed of the branched polymer, the crosslinked polymer, and the homopolymer of the multifunctional monomer. A small amount of homopolymer is produced because the concentration of the multifunctional monomer is low. There are mainly two structures in the final polymer:



As the ionization and excitation caused by radiation are random, crosslinking and degradation also occur randomly. The addition of a small amount of a multifunctional monomer only sensitizes radiation crosslinking, and it does not change the sort of reaction. Obviously, the multifunctional monomer will affect the radiation sensitivity of the PP chain after grafting on PP. However, it seems that the type of crosslinking reaction cannot be changed because the multifunctional monomer stays on the PP chain randomly just like the comonomer or radical on the PP chain. The model of random crosslinking is applicable to the crosslinking system with a multifunctional monomer in a certain dose range; therefore, the C-P equation is applicable in this situa-

**Table II Melting Strength of PP Before and After Radiation**

Elongation Ratio	Melting Strength ( $10^5$ MPa)	
	Before Radiation	After Radiation
1	0.023	0.025
2	0.28	0.45
3	0.54	1.37
4	0.98	2.29
5	1.52	3.20
6	1.81	4.07
7	2.27	5.07

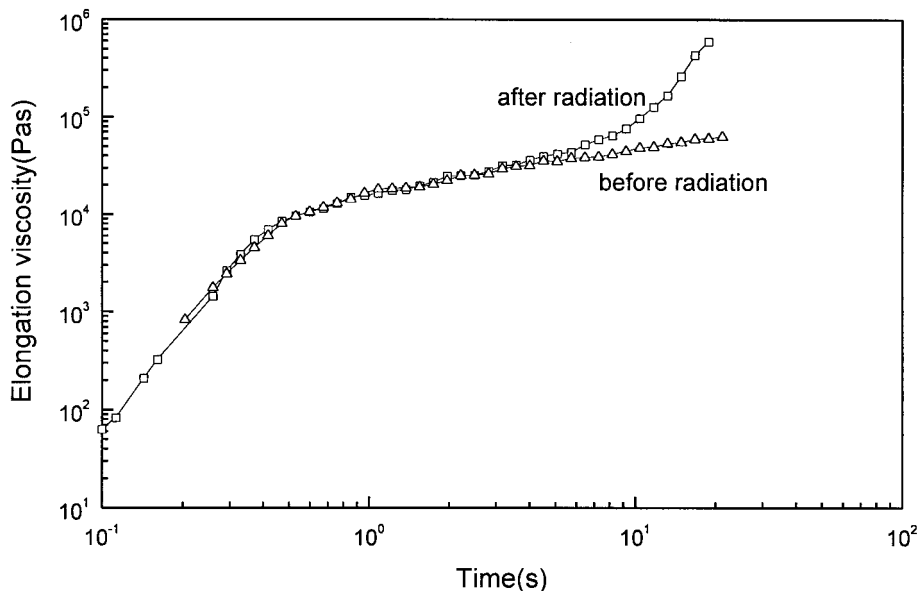


Figure 1 Elongation viscosity versus time.

tion. This article examines in detail on the application of the C-P equation in the radiation crosslinking of different kinds of PP with a multifunctional crosslinking agent in air. Furthermore, the crosslinking  $G$  value [ $G(x)$ ], scission  $G$  value [ $G(s)$ ],  $Rg$ , and so on are calculated.

EXPERIMENTAL

Materials

HPP had a number-average molecular weight ( $M_n$ ) of  $6.0 \times 10^4$ , a melting index (MI) of 2.0 g/10

min, and a  $\Delta H$  of  $-91.615 \text{ J/g}$  ( $\Delta H$  was determined by the following procedure: the sample was heated from room temperature up to  $190^\circ\text{C}$  at a rate of  $10^\circ\text{C/min}$ , held at this temperature for 5 min, and cooled from 190 to  $50^\circ\text{C}$  at a rate of  $10^\circ\text{C/min}$ ). IPP with 11.2 wt % ethylene had a  $M_n$  of  $6.8 \times 10^4$ , a MI of 2.0 g/10 min, and a  $\Delta H$  of  $-72.301 \text{ J/g}$  ( $\Delta H$  was determined by the same procedure used for HPP). RPP with 2.4% ethylene units had a  $M_n$  of  $7.1 \times 10^4$  and a MI of 6.7 g/10 min. PP-1 was a HPP with a MI of 4.2 g/10 min. The multifunctional crosslinking agent was trimethylolpropane triacrylate (TMPTA) or 1,6-hexanediol diacrylate (HDDA).

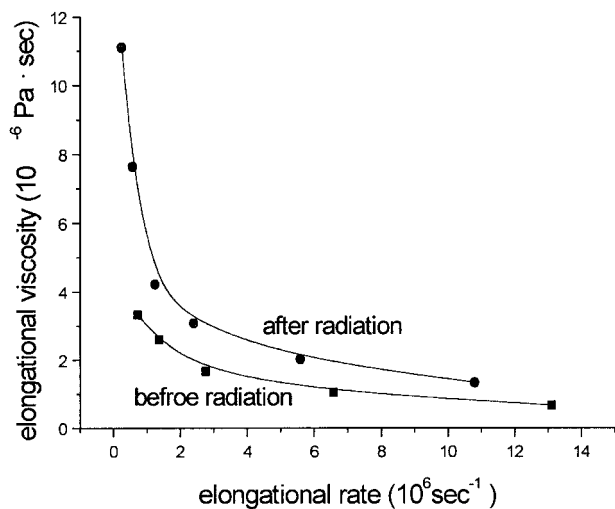


Figure 2 Relationship between elongation viscosity and elongation rate with a slenderness ratio of 5:1.

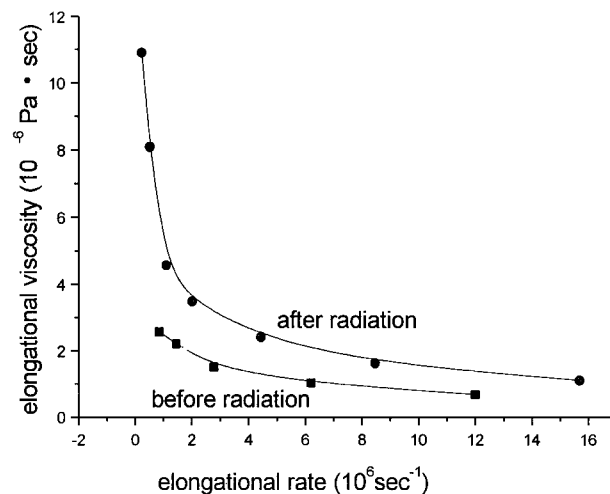
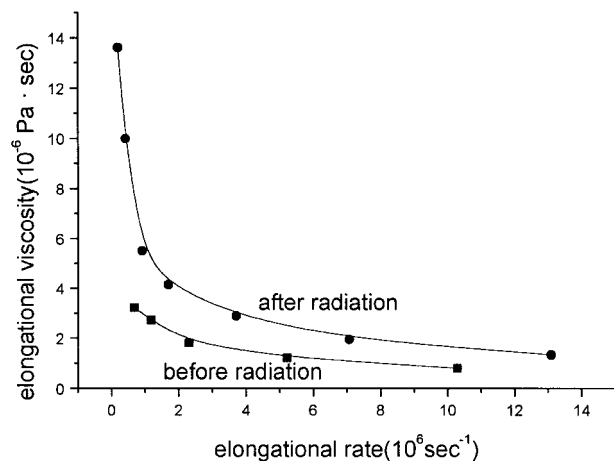


Figure 3 Relationship between elongation viscosity and elongation rate with a slenderness ratio of 10:1.



**Figure 4** Relationship between elongation viscosity and elongation rate with a slenderness ratio of 20:1.

### Preparation

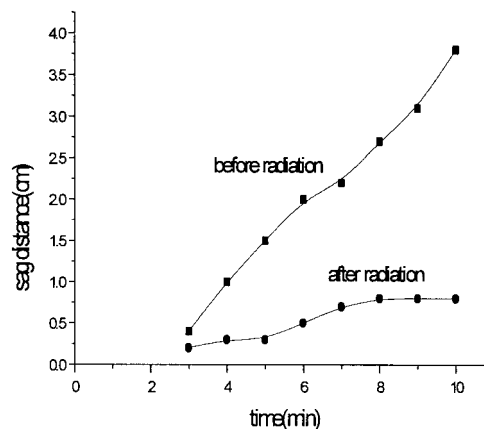
Irradiation was carried out at dose rate of 77 Gy/min

### PP Crosslinking

PP powder was mixed with the phenol antioxidant, TMPTA, and other additives. The mixture was then extruded in a single extruder. The pellet of the PPs with TMPTA were irradiated by  $^{60}\text{Co}$   $\gamma$ -rays in air. The pellet shape was a cylinder with a diameter of about 3 mm and a height of about 5 mm.

### PP Branching

PP powder was mixed with HDDA and other additives. The mixture was stored in a vacuum at room temperature for 48 h. Then, the PP powder with HDDA was irradiated by  $^{60}\text{Co}$   $\gamma$ -rays in a vacuum.



**Figure 5** Relationship between sag distance and time.

### Measurement

Gel fraction was measured by the immersion of about 0.1 g of sample covered with 120-mesh copper gauze in boiling xylene for 8 h, and gel fraction was calculated by the following formula: gel fraction (%) =  $w_2/w_1$  (where  $w_1$  is original sample weight and  $w_2$  is the gel weight after extraction with xylene).

$M_n$  was measured by gel permeation chromatography (PL220) at 135°C.

Melting strength was determined by Rheotens with an elongation acceleration of 20 mm/s<sup>2</sup>, and the melt temperature was 200°C.

Elongation viscosity versus elongation time was measured on a rheometer of melt elongation with a test specimen that was 60 × 7 × 1.5 mm. The specimen was held at 180°C for 7 min and then tested at this temperature with a strain rate of 0.2 s<sup>-1</sup>.

Elongation viscosity versus elongation rate was measured with a capillary rheometer according to the method of refs. 9 and 10.

**Table III** Gel Fraction (%) and Calculated Results of HPP with Different Amounts of TMPTA

TMPTA (%)	R (kGy)						Equation and <i>f</i>
	0.77	1.0	1.3	1.7	2.3	3.2	
0.5	6.9	20.6	41.1	46.3	48.3	54.8	$S + S^{1/2} = 0.85 + 0.79/R$ ( $f = 0.972$ )
1.0	24.5	41.0	46.9	49.2	55.6	61.3	$S + S^{1/2} = 0.79 + 0.65/R$ ( $f = 0.988$ )
1.5	24.5	37.3	43.3	51.1	57.6	62.4	$S + S^{1/2} = 0.81 + 0.62/R$ ( $f = 0.997$ )
2.0	16.2	37.6	40.7	48.3	61.3	63.2	$S + S^{1/2} = 0.82 + 0.61/R$ ( $f = 0.985$ )
2.5	25.3	41.0	46.9	49.2	55.6	61.3	$S + S^{1/2} = 0.70 + 0.58/R$ ( $f = 0.979$ )
3.0	25.2	39.4	48.4	58.0	63.5	70.9	$S + S^{1/2} = 0.71 + 0.59/R$ ( $f = 0.979$ )

**Table IV Gel Fraction and Calculated Results of IPP with Different Amounts of TMPTA**

TMPTA (%)	<i>R</i> (kGy)						Equation and <i>f</i>
	1.0	1.2	1.3	1.7	2.3	3.2	
0.5	28.3	38.7	44.8	49.2	57.9	60.2	$S + S^{1/2} = 0.64 + 0.99/R$ ( $f = 0.979$ )
1.0	32.3	41.2	45.8	56.9	64.6	—	$S + S^{1/2} = 0.52 + 0.97/R$ ( $f = 0.992$ )
1.5	32.2	46.0	—	50.6	59.6	65.2	$S + S^{1/2} = 0.61 + 0.96/R$ ( $f = 0.986$ )
2.0	36.1	52.9	—	59.5	66.4	74.4	$S + S^{1/2} = 0.48 + 0.92/R$ ( $f = 0.980$ )
2.5	31.3	45.8	48.3	59.8	—	63.3	$S + S^{1/2} = 0.64 + 0.81/R$ ( $f = 0.962$ )
3.0	46.3	49.2	55.8	60.0	63.2	65.0	$S + S^{1/2} = 0.75 + 0.52/R$ ( $f = 0.970$ )

## RESULTS AND DISCUSSION

### Properties of Crosslinked PP and Branched PP

Properties of crosslinked PP or branched PP, such as melting strength, can be increased a lot compared to neat PP. For example, after PP-1 with 0.3% HDDA was irradiated by 1 kGy  $\gamma$ -rays, branched PP was obtained, and its properties increased as shown.

The results for mechanical properties are shown in Table I. The results for melt strength are shown in Table II. The results for elongation viscosity versus elongation time are shown in Figure 1. The results for elongation viscosity versus elongation rate are shown in Figures 2–4. The experiment of melt sag were carried out at 190°C; the result is shown in Figure 5.

### Radiation Crosslinking Behavior of the Different Kinds of PP with a Multifunctional Crosslinking Agent

HPP, IPP, and RPP with different amounts of TMPTA were irradiated in a dose range of 0.75–4 kGy. The results are shown in Tables III–V.

The correlation coefficients (*f*s) of linear regression were all above 0.97; therefore, the C–P equation seemed applicable for the radiation crosslink-

ing of HPP with different concentrations of TMPTA in a certain dose range.

Similar results were obtained for IPP and RPP as for HPP. The C–P equation seemed not only applicable for the radiation crosslinking of HPP but also for the radiation crosslinking of IPP and RPP with different concentrations of TMPTA in a certain dose range.

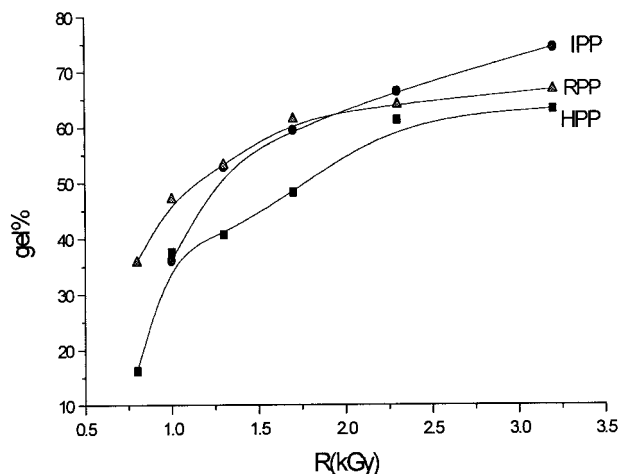
### Results Comparison of the Different PPs

Three different PPs with TMPTA were irradiated, and the results are shown in Figures 6 and 7.

It can be seen from Figure 6 that copolypropylene had a higher gel fraction than HPP at the same concentration of TMPTA. This can be explained by the structure and nature of the different PPs. It is known that polyethylene prefers to crosslink. Copolypropylene prefers to crosslink while being irradiated because there are more ethylene units in copolypropylene. Furthermore, radicals caused by radiation exist in a crystal phase, an amorphous phase, and an interfacial phase. The crosslinking of PP takes place mainly in the amorphous phase, whereas degradation occurs in the interfacial phase.<sup>11</sup> As copolymer has more amorphous phase, it is easier to crosslink and produce a higher gel fraction. Figure 7 indicates that HPP had a higher ratio of  $P_0/q_0$  than

**Table V Gel Fraction and Calculated Results of RPP with Different Amounts of TMPTA**

TMPTA (%)	<i>R</i> (kGy)							Equation and <i>f</i>
	0.62	0.81	1.0	1.3	1.7	2.3	3.2	
1.0	12.2	22.2	43.4	51.7	54.3	58.4	63.7	$S + S^{1/2} = 0.73 + 0.68/R$ ( $f = 0.980$ )
1.5	16.4	32.4	46.3	53.9	58.5	59.4	—	$S + S^{1/2} = 0.67 + 0.66/R$ ( $f = 0.983$ )
2.0	15.3	35.8	47.1	53.2	61.4	64.0	66.7	$S + S^{1/2} = 0.68 + 0.63/R$ ( $f = 0.993$ )
2.5	24.5	38.0	53.5	56.5	62.7	67.5	—	$S + S^{1/2} = 0.69 + 0.52/R$ ( $f = 0.982$ )
3.0	25.9	37.5	50.4	60.7	64.8	69.5	72.1	$S + S^{1/2} = 0.66 + 0.52/R$ ( $f = 0.987$ )

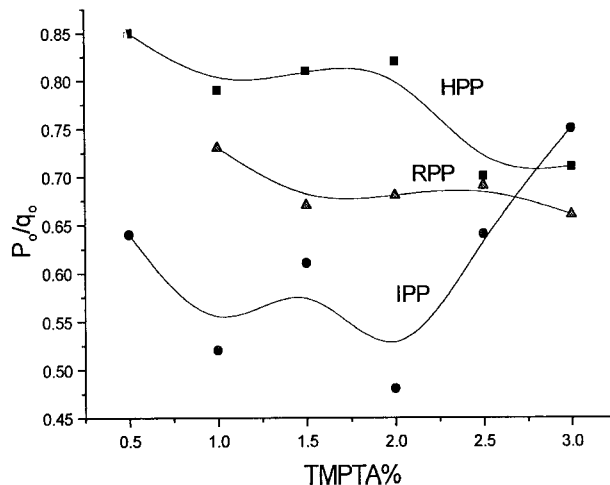


**Figure 6** Relationship between gel fraction and  $R$  for the three different PPs with 2% TMPTA.

copolypropylene with TMPTA from 0.5 to 2.0%. This also proves that copolypropylene was easier to crosslink than HPP.

The results of the calculated crosslinking and scission parameters of the three kinds of PP with the C-P equation are shown in Table VI, in which  $w$  is the average molecular weight of chain units.

It is obvious that IPP had the highest  $R_g$  and  $G(x)/G(s)$  values among the samples that were studied; therefore, IPP was the best material for radiation branching among the samples of HPP, IPP, and RPP studied. IPP was also the best material for radiation crosslinking among the samples of HPP, IPP, and RPP studied because it



**Figure 7** Relationship between  $P_j/q_0$  and the concentration of TMPTA.

had the highest  $G(x)/G(s)$  value and the highest gel fraction after  $R$  was over 2.5 kGy.

## CONCLUSIONS

1. Crosslinking and branching can increase properties of PP such as melting strength.
2. The C-P equation seems applicable to the radiation crosslinking of PP, including HPP, RPP, and IPP, in the presence of a multifunctional crosslinking agent within a certain dose range in air.

**Table VI** Crosslinking and Scission Parameters of the Three Kinds of PP

	$w$	$M_n$ ( $10^4$ )	$\mu$	TMPTA (%)	$q_0 \times 10^3$	$P_0 \times 10^4$	$G(x)$	$G(s)$	$G(x)/G(s)$	$R_g$ (kGy)
HPP	42.0	6.0	1437	1.0	1.07	8.45	122	193	0.63	0.54
				1.5	1.12	9.07	128	207	0.62	0.52
				2.0	1.14	9.35	130	261	0.50	0.52
				2.5	1.20	8.40	137	192	0.71	0.45
				3.0	1.18	8.38	135	191	0.71	0.46
IPP	40.4	6.8	1636	1.0	0.630	3.28	74.9	77.9	0.96	0.66
				1.5	0.637	3.89	75.7	92.4	0.82	0.69
				2.0	0.664	3.19	78.9	75.8	1.04	0.61
				2.5	0.745	4.69	88.5	111	0.80	0.60
				3.0	1.18	8.85	140	210	0.67	0.42
RPP	41.5	7.1	1704	1.0	0.863	6.30	99.8	145	0.67	0.54
				1.5	0.889	5.96	103	138	0.75	0.50
				2.0	0.932	6.33	108	146	0.74	0.48
				2.5	1.13	7.79	131	180	0.73	0.40
				3.0	1.13	7.44	131	172	0.76	0.38

3. IPP is the best material for radiation branching and radiation crosslinking of PP among the samples of HPP, IPP, and RPP studied.

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