# Effect of Chain Structure on the Melt Rheology of Modified Polypropylene

# MASATAKA SUGIMOTO,<sup>1</sup> TADASHI TANAKA,<sup>2</sup> YUICHI MASUBUCHI,<sup>1</sup> JUN-ICHI TAKIMOTO,<sup>1</sup> KIYOHITO KOYAMA<sup>1</sup>

<sup>1</sup> Department of Materials Science and Engineering, Yamagata University, Jonan 4-3-16, Yonezawa, 992 Japan;

<sup>2</sup> Chisso Petrochemical Corporation Polymer Research Center, 5-1, Goi Kaigan, Ichihara, Chiba, 290 Japan

Received 6 May 1998; accepted 12 December 1998

ABSTRACT: The effect of molecular structure of polypropylene (PP) on the melt rheological properties were investigated for electron irradiated polymer and di-2-ethylhexyl peroxy dicarbonate (EHPC)-treated polymer. The modifications were examined in terms of the rheological behaviors, molecular weight distribution, and the degree of branching. The high melt strength PP was obtained by irradiating with 50 and 80 kGy and adding EHPC. The modified PPs showed the strain hardening in the uniaxial elongational viscosity, though the linear elongational viscosity was lower than that of the unmodified PP. Low angle laser light-scattering measurements of the modified PPs showed the interesting results; high irradiation doses such as 50 and 80 kGy caused higher molecular weight chains branching. Nevertheless, the long branching chains were not detected for the EHPC modified PP, which also showed the strain hardening in uniaxial elongational flow. In this article, the relation between chain structure and rheological properties is discussed. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 73: 1493–1500, 1999

**Key words:** polypropylene; electron beam irradiation; EHPC treatment; elongational viscosity; long chain branches

## **INTRODUCTION**

The linear polypropylene (PP) of commerce has many desirable and beneficial physical properties such as stiffness, resistance to corrosive chemicals, nonenvironmental pollution when incinerated, and low specific gravity. Therefore PP has been expected in various applications instead of polyvinylchloride, polyurethane, polyethylene, and so on. However, PP is a linear polymer, which exhibits low melt strength and weak strain hardening behavior. One of the effective approaches to achieve the high melt strength is adding long chain branches onto backbone species. It is possible to crosslink PP using irradiation of electron beams.<sup>1,2</sup> The crosslinking results from the formation of the network structure due to macroradical combinations during the irradiation. It is reported that the electron beam irradiation leads to branching structure of polyethylene and PP; the effect of the structure is very evident in foaming articles.<sup>1</sup> As for the high melt strength PP modified via irradiation, the effect of polyfunctional monomers on the melt strength and the thermal behavior has been examined.<sup>2,3</sup> The polyfunctional monomers with shorter molecular chains are the most effective for enhancing the melt strength. It is suggested that a few higher molecular weight chains formed by the irradiation, induced entanglement of molecular chains of

Correspondence to: K. Koyama.

Journal of Applied Polymer Science, Vol. 73, 1493–1500 (1999) © 1999 John Wiley & Sons, Inc. CCC 0021-8995/99/081493-08

Sample	Irradiation Dose (kGy)	EHPC (wt %)	MFR g/10 min	<i>M</i> <sub>n</sub> (/10 <sup>4</sup> )	<i>M</i> <sub>w</sub> (/10 <sup>5</sup> )	<i>M</i> <sub>z</sub> (/10 <sup>5</sup> )	$M_w/M_n$	$M_z/M_w$
А	10	_	4.8	7.3	3.4	7.7	4.6	2.3
В	50	_	2.7	4.7	5.5	22.1	11.7	4.0
С	80	_	4	5.3	5.8	27.7	10.8	4.8
D (control)	_		2.0	4.3	3.6	8.6	8.4	2.4
Е	_	1.2	4.1	4.4	3.5	11.5	7.8	3.3

 Table I
 Molecular Characterization of the Samples

EHPC, di-2-ethylhexyl peroxy dicarbonate; MFR, melt flow rate.

PP, led to the higher melt strength. The addition of peroxide is also used to prepare graft or branch modified resins.<sup>4–6</sup> Peroxide initiator with a high concentration can produce crosslinked PP up to 90 wt % gel materials.<sup>4</sup> It also has been reported that functional monomers under a presence of free radicals produce more stable macroradical sites,<sup>6</sup> which increase the likelihood of undergoing further reactions owing to a decrease of the probability of fragmentation. The use of styrene as grafting chain onto PP under the presence of free radical initiators has been examined to improve the strain hardening behavior in the uniaxial elongation.<sup>5</sup> With increasing peroxide initiator, grafted PP using styrene with a constant concentration showed the strain hardening and an increase of storage modulus G' because of an increase of entanglement between molecular chains. Wong<sup>6</sup> studied a family of glycidyl methacrylate and styrene graft modified PP; the low frequency dynamic response is influenced by the type of initiator, concentration of monomer, and the use of comonomer.

Numerous attempts have been made to investigate the role of long chain branches for nonlinear rheology features.<sup>1,2,5–8</sup> Nevertheless, a number of obscure points about the effect of modifications on the strain hardening behavior of polymer melts still remains. Nonlinear rheology of branching polymers is most often discussed as entanglement of molecular chains which result in a weaker strain dependence of the dumping function.<sup>9,10</sup> There are, however, some evidences that differ from the studies that the strain hardening is caused by a presence of long chain branches.<sup>11,12</sup>

The purpose of this article is to consider how the melt rheology is influenced by the chain structure of modified PP prepared with electron beam and di-2-ethylhexyl peroxy carbonate (EHPC) which decomposed at a relatively low temperature. From the shear, elongational behaviors and the branching number, we discussed a relationship between the rheology and the chain structure for modified PPs.

# **EXPERIMENTAL**

# Materials

The PP powders were supplied by Chisso Petrochemical Corporation (Chiba, Japan). The natural samples (before modification) are homopolymer resin with a melt flow rate (MFR) of 0.5 and 6 g/10 min at 230°C. Conventional homopolymer resins with MFR of 2 and 5.2 g/10 min were used as a control.

# Preparation of Modified PP

Molecular properties of the samples are shown in Table I. We modified the linear PP by two methods: the electron beam irradiation and the addition of EHPC. The irradiation was performed using Cockroft Walton type accelerator in Takasaki Institute of Japan Atomic Energy Research Institute. The sample (MFR was 0.5 g/10 min at 230°C) was irradiated under nitrogen atmosphere with an electron beam; the beam current was 1 mA, the acceleration energy was 2 MeV, and the irradiation doses were 10, 50, and 80 kGy. After the irradiation, the samples were heated for 30 min at 80°C and further heated for 60 min at 130°C to react the residual radicals. EHPC was added under nitrogen atmosphere to the PP in which MFR was 6 g/10 min. The mixture was annealed for 30 min at 130°C and further kept for 60 min at 130°C to react residual radicals. After the irradiation and the EHPC treatment, phenoltype antioxidant (0.2 wt %) was added to the powders. The mixtures were pelletized using a single-screw extruder at 230°C.

#### **Rheological Measurements**

The examined rheological properties were melt strength, swell ratio, dynamic viscoelasticity and uniaxial elongational viscosity. The melt strength and the swell ratio were measured by Capilograph (Toyoseiki Co. Ltd., Tokyo, Japn) having an orifice of 2.095 mm. The melt strength was measured after keeping the samples at 230°C for 5 min. The extrusion rate and the take-up velocity were 20 mm/min. The swell ratio was obtained from the ratio of the extrudate diameter to the orifice, which was extruded in the same way with the melt strength measurement. MFR was obtained by weighing the flowed PP for 10 min under 0.212 N at 230°C using a melt flow indexer (Toyoseiki Co. Ltd.). Shear viscoelastic measurements were performed by RMS-800 (Rheometric Scientific F. E. Ltd., Tokyo, Japan). Parallel plates 25 mm in diameter and 2 mm in the gap height, were used for the frequency sweep. The test specimens were cut from a sheet that had been prepared by compression moulding at 230°C. The frequency range was 0.1 to 100 rad/s, and the maximum strain was fixed at 5%. We confirmed that these conditions were within the linear viscoelastic region. For uniaxial elongational viscosity measurement, the polymer melts were extruded at a rate of 5 mm/min to sample rods at 210 through a die with a single orifice of 2.095 mm in diameter (Capilograph, Tovoseiki Co. Ltd.). The rods had a diameter of 3 to 4 mm and a length of 30 mm. To eliminate residual strain of the samples, 10 min of equilibration time was allowed before measurements. Using these rods, uniaxial elongational viscosity at constant strain rates was measured by Meissner-type rheometer<sup>13</sup> (Toyoseiki. Co. Ltd.). By a CCD video camera, we confirmed the uniform elongation and calculated the actual strain rates.

#### Characterization of the Chain Structure

The degree of chain branching affects the physical properties of the polymer. Many studies on the theory of the branching polymer solution have been made already,<sup>14–16</sup> but the assessment of randomly branching chains often lacks in reliability because of broad distribution of the molecular weight and randomness of chain branching. In recent years, however, the study for a dilute solution has been advanced as a result of progresses in theory, devices, and polymerization method. Several articles have been devoted to the study of random branches.<sup>2,17–20</sup> Dilute solution behavior

for the randomly branching polymer is argued as a relationship between the branch structure and the parameters related with the molecular size: mean square gyration radius, intrinsic viscosity, and hydrodynamic radius. We estimated the degree of chain branching  $\lambda$  from the mean-square gyration radius according to Zimm and Stockmayer.<sup>14</sup> A theory for the intrinsic viscosity of a branching polymer presented by Zimm and Kilb, should be limited to the type of star branching chain (Yau, W. W., unpublished data).<sup>15</sup> The method proposed by Zimm and Stockmayer<sup>14</sup> is straightforward in principle, but the effect of branch on the mean-square radii of gyration is often screened with the effect of molecular weight distribution of the branching polymer. Therefore, the samples were fractionated to five components using gel permeation chromatography (GPC) for the purpose of improving experimental accuracy. The  $\lambda$  of broad molecular weight distribution (MWD) sample considerably differs from one of narrow MWD sample owing to a breadth of the GPC chromatograph peak.

Degree of branching is given by  $\lambda$ , which is represented by the molecular weight M and the branching points m as:

$$\lambda = m/M. \tag{1}$$

 $\lambda$  can be determined as following procedure by the measurement of the molecular size of linear and branching chains, when the two polymers comprise the same molecular weight and chemical sort. In the  $\theta$  solvent, the ratio of the mean square gyration radius of branching polymer  $\langle S_0^2\rangle_b$  to that of linear polymer  $\langle S_0^2\rangle_l$  was represented by g known as Zimm-Stockmayers branch parameter  $g^{14}$ 

$$g = \langle S_0^2 \rangle_b / \langle S_0^2 \rangle_l \tag{2}$$

Equation 2 offers that the degree of branching can be estimated from light-scattering measurements. We assumed that the modified PPs are the tri-functional random branch polymers as well as low density polyethylene. Regarding tri-functional random branching polymer, it is known that g is expressed in terms of the degree of branching as (Yau, W. W., unpublished data):

$$g = \left[ \left( 1 + \frac{\lambda M}{7} \right)^{1/2} + \frac{4\lambda M}{9\pi} \right]^{-1/2}$$
(3)

Sample	Irradiation Dose (kGy)	EHPC (wt %)	MFR g/10 min	Melt Strength (cN)	Swell Ratio	Activation Energy $(J/mol \cdot K)$
A	10	_	4.8	1.1	1.5	3.8
В	50		2.7	8.5	1.8	5.7
С	80		4	12	2.2	6.1
D (control)	_		2.0	1.7	1.5	3.7
Е	_	1.2	4.1	5.1	1.8	4.9

Table II Melt Properties and Melt Strength Measured at 230°C

EPHC, di-2-ethylhexyl peroxy dicarbonate; MFR, melt flow rate.

and furthermore from the relationship between chain size and molecular weight, g was represented as Equation 4.<sup>21</sup>

$$g^{1/2} = \left(rac{M_{l,i}}{M_{b,i}}
ight)^{a+1}$$
 (4)

where *a* was 0.75, quoted from H. Coll.<sup>22</sup>  $M_{l,i}$  and  $M_{b,i}$  were the molecular weight of the i-th particular eluted fraction of the linear polymer and the branching polymer, respectively. The polymer solution flowed from GPC causing light-scattering in low angle laser light scattering (LALLS) unit; the molecular weight is obtained from the intensity—*g* is calculated from Equation 4, thereby giving  $\lambda$  from Eq.3.

In the size exclusion and the LALLS measurements, 0.1 g of polymer was completely dissolved in 100 cc of ortho-di-chlorobenzene (ODCB) containing 0.1 wt % butyl hydroxy toluene. The samples were injected into Waters 150 chromatograph operating at 135°C and



**Figure 1** Storage modulus G' plotted against frequency.

flowed at a rate of 0.8 ml/min. Detection was made by observing changes of the refractive index and LALLS; wave length was 633 nm (He-Ne light source).

#### RESULTS

#### **Rheological Properties**

As the electron beam irradiation dose increased, the melt strength and the swell ratio increased (see Table II). MFR of modified PP was higher than that of the unmodified PP. Among irradiated PPs, irradiated PP with 50 kGy showed relatively lower MFR.

Dynamic viscoelastic measurements were reproduced within 6% standard deviation to the acquired data. The storage modulus G' plotted as a function of frequency is shown in Figure 1 for modified PP with various levels of irradiating doses and EHPC. G' was decreased by the electron beam irradiation more than unirradiated PP.



**Figure 2** Complex viscosity  $\eta^*$  plotted against frequency.



**Figure 3** Time development of elongational viscosity  $\eta_{\rm E}$ .

The irradiated PP with 10 kGy showed the strongest dependence on frequency. The slope of G' for modified PP (50 and 80 kGy) was almost the same, but seemed to be smaller than that of unmodified PP in the low frequency tested. The decrease in G' was also observed for the EHPCmodified PP. Among the modified PPs with the irradiation and the peroxide, 50 kGy-modified PP showed high elasticity in the frequencies less than 10 rad/s. The complex viscosities  $\eta^*$  of modified PP were lower than those of unmodified PP (see Fig. 2). PP modified with 10 kGy led to the presence of a plateau at low frequencies, as  $\eta^*$ approached the limit of zero shear viscosity  $\eta_0$ . Figure 3 shows elongational viscosity at constant strain rates at 180°C. Within the strain rates examined, the elongational viscosity  $\eta_{\rm E}$  of the conventional PP and modified PP with 10 kGy did not show the strain hardening, whereas those of the modified PPs (50 and 80 kGy) did. The irradiation and the EHPC treatment were found to have a pronounced effect on the increase of the nonlinear elongational viscosity  $\eta_{\rm E(nonlinear)}$  of PP, which spanned 1 to 2 decades for the linear elongational viscosity  $\eta_{\rm E(linear)}$ . As the irradiation dose increased to 50 kGy and over, the strain hardening behavior was hardly influenced by the irradiation, though  $\eta_{\rm E(linear)}$  decreased.

#### **Molecular Structure**

Table III indicates that the high irradiation (50 and 80 kGy) caused long chain branching. And the higher molecular weight components were composed of the higher branching number m and degree of chain branching  $\lambda$  (see Table III and Fig. 4). On the contrary, the irradiated PP with 10 kGy showed much lower  $\lambda$  and *m* than the irradiated PP with 50 and 80 kGy. The width of the MWD for 10 kGy irradiated PP was narrower than that of the unirradiated PP (see Fig. 5). However, when the irradiation dose was increased and the MWD was broadened to both the low and high end of that, there was a marked increase of high molecular weight chains (50 and 80 kGy), though the peaks of the MWD curves were shifted to lower molecular weight (see Fig. 5 and Table 3).

The branching chain for the EHPC modified polymer was not detected by LALLS. Figure 6 shows that MWD of EHPC-treated PP was broader than that of unmodified PP, but there was no apparent increase of the high molecular

Table III Effect of Electron Beam Irradiation Dose on Amount of Branching

	Molecular Weight $(M)$ of Each Fraction $(/10^4)$				Branching Degree		Branching			
	A (10 kGy)	B (50 kGy)	C (80 kGy)	D (control)	$(\lambda) (/10^{-5})$			Number (m)		
Eluted Fraction					А	В	С	Α	В	С
Fr. 1	260	370	430	250	0.08	2.5	7.3	2.1	95	320
Fr. 2	120	150	170	110	0.19	2.7	6.0	2.3	42	104
Fr. 3	54	62	66	51	0.54	2.8	4.7	2.9	17	31
Fr. 4	23	24	25	21	1.7	2.7	3.3	3.9	6.7	8.2
Fr. 5	9.6	9.0	8.8	8.7	5.1	2.0	0.83	4.8	1.8	0.7



Figure 4 Branching number against molecular weight.

weight component that was observed in the highly irradiated samples.

# DISCUSSION

#### **Effect of Electron Beam Irradiation**

We considered that the electron beam irradiation has two effects on the molecular structure: reduction of the molecular weight and production of the long chain branching. Due to the chemical nature of PP, it has a tendency to undergo  $\beta$ -scission under a presence of radicals. This causes a decrease of the molecular weight<sup>6,23</sup> so that an increase of MFR and a decrease of G',  $\eta^*$ , and  $\eta_{\text{E(linear)}}$ are reasonable (see Table I and Fig. 1–3). On the



**Figure 5** GPC-LALLS curves for modified PP prepared with increasing irradiation dose.

other hand, as shown in Figure 3, the modified PPs, except 10 kGy-irradiated PP, showed the strain hardening. This type of behavior is typically reported for LDPE,<sup>7,24</sup> graft-modified polymers with long chain branches,<sup>1,2,5</sup> and crosslinked materials. The presence of high molecular weight branching chains for irradiated PP with 50 and 80 kGy, which showed the strain hardening, was obviously exhibited by LALLS (Table III). This suggests that increased free radicals, promoted by the irradiation, made branching reactions more probable. The irradiated PP with 80 kGy showed higher MFR, and lower G',  $\eta^*,$  and  $\eta_{E(linear)}$  than those of 50 kGy-irradiated PP. Under this condition, the effect of chain scission was more dominant than the crosslinking reaction. The irradiated PP prepared with the lowest electron beam irradiation (10 kGy) showed higher MFR, lower G' and  $\eta^*$  at the lower frequency range, and the strain hardening behavior was not evident. Furthermore, LALLS measurements showed that the 10 kGy-irradiated PP was composed of the narrower MWD, and of few branching chains. Under this condition, the rate of macroradical combination would be much slower than the rate of chain scission. It has been reported that a small quantity of a peroxide added to PP in postreactor decomposes preferentially high molecular weight chains and narrows the molecular weight distribution.<sup>25</sup> The low electron beam irradiation resulted in the production of fewer PP radicals, making crosslinking less probable. It follows from what has been mentioned that the strain hardening behavior of irradiated PP is governed by the long chains branching and not by the short chains branching.



Figure 6 Similar to Figure 5 for EHPC-modified PP.

#### **Effect of Addition of EHPC**

The addition of EHPC to pure PP decreased melt flow rate (6 to 4.1 g/10 min), indicating an increase of the molecular weight.<sup>23</sup> The content of gel with insoluble three dimensional network extracted in boiled xylene, was less than 0.1 wt %. The relationship between the molecular weight and the mean square radius of gyration in 1,2,4trichrolobenzene was almost similar to that of unmodified PP. This implies that the long branching chain was not produced. Furthermore, higher molecular weight component formed by intermolecular combination was not evident as shown in Figure 6. The modified PP prepared with EHPC showed, however, the higher melt strength and the strain hardening (see Table II and Fig. 3). This is contrary to the pronounced view that the strain hardening behavior of the elongational viscosity results from entanglement of the branching or the grafted chains. A possible explanation for the discrepancy between the rheological data and the results of LALLS could be that the strain hardening behavior was caused by a small quantity of extremely high molecular weight chains which was impossible to evaluate by  $\text{GPC}^{11,24,26,27}$ We shall return to this point later. Otherwise, the level of branching was not severe enough to evaluate in the LALLS measurement.

#### Effect of the Modifications on the Strain Hardening

The shear and the elongational measurements have been observed for the branch and graft polymers.<sup>1,2,5,6-8</sup> It has been reported that the highly branching polymers exhibit a weaker damping function,  $^{9,10}$  leading to sharp upturn of the elongational viscosity. However, some studies did show the strain hardening in linear polymers,<sup>11,12</sup> explained by introduction of a small amount of the extremely long relaxation time mode into the normal relaxation spectrum.<sup>12,28,29</sup> Noteworthy is that the EHPC-modified PP, for which no long branches were detected, also showed the strain hardening. From a theoretical consideration, the strain hardening properties are represented by the damping function and the relaxation spectrum.<sup>30,31</sup> Since the damping function is affected by a presence of the branches,<sup>32</sup> we consider that the elongational properties of the modified PP prepared with EHPC were affected by the long relaxation time resulting from a few ultra-high molecular weight chains.

# CONCLUSION

The modified PPs prepared with the electron beam and EHPC showed good melt strength and strain hardening. The rheological properties for irradiated PP were greatly influenced by a competition between  $\beta$ -scission and crosslinking reactions, depending on the irradiation dose. The strain hardening of the irradiated PP resulted from constraint of the chain relaxation owing to a presence of branching molecules. On the other hand, the long chain branching for the EHPCmodified PP was not evident, though the strain hardening was intensified. We consider that this is because of a small amount of ultra high molecular weight polymer. Further work is required on the basis of this article to determine how the modifications presented herein affect the relaxation spectrum and the damping function.

This work was supported by Dr. Yoshii at Japan Atomic Energy Research Institute. The authors thank him for materials preparer in electron beam irradiation and valuable comments.

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