Long-Chain Branching of Polypropylene by Electron-Beam Irradiation in the Molten State

B. Krause, M. Stephan, S. Volkland, D. Voigt, L. Häußler, H. Dorschner

Leibniz Institute of Polymer Research Dresden, Hohe Straße 6, 01069 Dresden, Germany

ABSTRACT: The electron-beam irradiation of polymers generates modification effects in the macromolecular structure and material properties. Therefore, irradiation processing is mostly realized in the polymer solid state. In this way, the modification of linear polypropylene may result in long-chain branching of polypropylene macromolecules. The objective of this article is to investigate the effect of a polymer in the molten state during electron-beam irradiation on the macromolecular structure and material properties of polypropylene. For this procedure, a special irradiation vessel (BG3) has been developed in which a rapid transfer of polymer films from the solid state to the molten state and a defined temperature during electron-beam irradiation are realizable. The irradiated samples have been analyzed by high-temperature size exclusion chromatography coupled with a multi-angle laser light scattering detector and differential scanning calorimetry (DSC) measurements. With an increasing irradiation dose, a high reduction of the molar mass and an increasing amount of long-chain branching are found. Compared with irradiation in the solid state, the modification in the molten state leads to a higher degree of branching. The rheological experiments in elongation flow clearly exhibit the existence of long-chain branching. Furthermore, DSC measurements show that the glass-transition temperature and peak temperatures of melting and crystallization decrease. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 99: 260–265, 2006

Key words: branched; chromatography; differential scanning calorimetry (DSC); electron beam irradiation; poly(propylene) (PP)

INTRODUCTION

Long-chain-branched polypropylenes (PPs) possess advantageous properties that are important in many industrial applications, such as good thermoforming behavior, high melt strength, and a uniform fine cell structure of extruded foams.[1,2] The optimization of the processing of this material depends on the rheological properties of the melt, which are strongly affected by the molar mass, molar mass distribution, and presence of long-chain branching (LCB). One way to create LCB in the linear polymer without additives is modification by electron-beam irradiation. Irradiation at room temperature is described, for example, in refs. 3–9. The latter has a distinct influence on the rheological properties, such as the elongational and shear viscosity, flow activation energy, and melt elasticity.[10,11] LCB, on the other hand, affects strongly the molecular structure and light scattering properties of the molecules.

Influence of LCB on the light scattering properties of the molecules

Polymer molecules are fractionated by size exclusion chromatography (SEC) according to their hydrodynamic volume. The size of a molecule depends on its molar mass and density in the dissolved state. Long-chain-branched molecules have a denser structure than linear molecules at the same molar mass, and the density depends on the number and type of branches. By the coupling of SEC with multi-angle laser light scattering (MALLS), molar mass M of every slice of a chromatogram can be determined absolutely without any calibration. Additionally, light scattering data give information about the mean-square radius of gyration ($\langle s^2 \rangle$) of the molecules with respect to branching with theoretical considerations.[12] The ratio of the mean-square radius of gyration of a branched polymer ($\langle s^2 \rangle_{\text{branch}}$) to that of a linear polymer ($\langle s^2 \rangle_{\text{linear}}$) is represented by g, which is known as the Zimm–Stockmayer branching parameter:[12]

$$g = \frac{\langle s^2 \rangle_{\text{branch}}}{\langle s^2 \rangle_{\text{linear}}} \qquad (1)$$

The coil of a branched chain is more compact than a linear one of the same molar mass, and so this factor g will be lower than 1 for a branched polymer. g gets smaller with an increasing degree of branching.
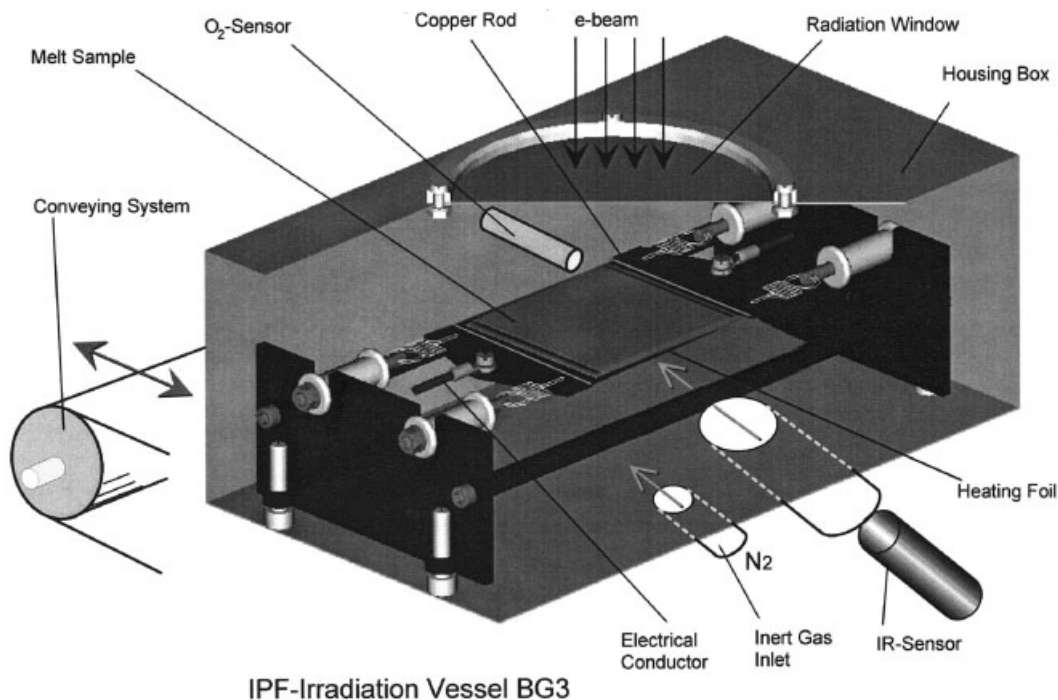
Figure 1   Irradiation vessel BG3 for the electron-beam irradiation of polymer films in the molten state.

For modified isotactic polypropylene (iPP), a tri-functional, randomly branched architecture can be assumed.[13] For such a trifunctional, randomly branched polymer, g is expressed in terms of the degree of branching as follows:

$$g = \left[\left(1 + \frac{m}{7} \right)^{0.5} + \frac{4m}{9\pi} \right]^{-0.5} \qquad (2)$$

where m is the number of branching points along the molecule.

Irradiation in the molten state

The formation of chain branching or crosslinking is located mainly in the amorphous regions. The material in the molten state contains no crystalline regions. This leads to the conclusion that all chains are available for branching reactions.[14] Therefore, the chance of chain branching during irradiation in the molten state of the material is much higher than in the solid state. In the solid state, the branching reactions are limited by the diffusion of chain fragments. Moreover, the thermal degradation of the molecular weight at high temperatures is enhanced.[15]

The temperature dependence of irradiation-induced reactions of polyethylene was described by Wu et al.,[15] Qu and Ranby,[16] and Dijkstra et al.[17] Already, the irradiation of polyethylene at room temperature can lead to the formation of insoluble parts by crosslinking. With the irradiation of polyethylene in the molten state, more crosslinked substances are obtained. A concentration of gel up to 90% for low-density polyethylene is possible.[15]

EXPERIMENTAL

Materials

The iPP homopolymer used in this study was Novolen PPH2150 (Basell Polyolefins Co. N.V., Hoofddorp, The Netherlands). According to the data sheet, the melt flow index was 0.3 g/10 min (230°C; 2.16 kg), and the density at room temperature was 0.90 g/cm^3. The iPP films (0.5 mm thick) were laboratory-scale-manufactured by conventional cast film extrusion processing.

Electron-beam irradiation

The iPP films were irradiated with 1.0 MeV with the electron-beam accelerator ELV-2 (Budker Institute of Nuclear Physics, Novosibirsk, Russia), as described in detail by Dorschner et al.[18] For electron-beam irradiation in the molten state, a special irradiation vessel (BG3) has been developed in which a rapid transfer of polymer film samples from the solid state to the liquid/melt state according to industrial pellet melting processes and the control of a defined melt temperature during electron-beam irradiation are realizable.[19] The BG3 (Fig. 1) includes a metal heating foil as a polymer film sample support and a temperature sensor for temperature control. The heating procedure is

controlled by a special X-ray-resistant infrared sensor (Raytech Corp., Shelton, CT) and self-designed temperature-controlling equipment. The samples were located on the supporting heating metal foil between two 50-μm-thick infusible and highly radiation-resistant polyimide films of the Kapton type (DuPont, Bad Homburg, Germany) to ensure close contact with the heating foil to facilitate the polymer melting process and otherwise prevent unacceptable adherence. The time needed for transferring the polymer samples from the solid state to the molten state was about 3–4 min. The electron-beam irradiation was carried out at 25°C and at a melt temperature of 200°C up to an irradiation dose of 100 kGy in an air environment.

Characterization

SEC

The molecular characterization of PP was carried out by high-temperature SEC. The instrument was a PL-GPC220 (Polymer Laboratories, Ltd., Shropshire, UK) at 150°C equipped with a refractive-index detector and coupled with a MALLS detector (Dawn EOS, Wyatt Technology Corp., Santa Barbara, CA). The column set consisted of two columns (PL mixed-B-LS, 300 mm × 7.5 mm, 10-μm pore diameter, Polymer Laboratories). The flow rate was 1 mL/min. The eluent was 1,2,4-trichlorobenzene (Merck KGaA, Darmstadt, Germany) stabilized with diphenylamine (Merck) against the thermooxidative degradation of PP. The calculations of the molecular parameters (weight-average molecular weight, number-average molecular weight, molar mass distribution, and radius of gyration) were carried out from the SEC data with commercial software (Astra 4.73, Wyatt Technology).

Differential scanning calorimetry (DSC)

The DSC measurements were performed on a Q1000 (TA Instruments, New Castle, DE) coupled with an autosampler in the temperature range of −60 to 210°C at a scanning rate of ±10 K/min. Samples of about 5 mg were investigated under a nitrogen atmosphere in a run cycle of first heating, cooling, and second heating. The calibration of the temperature and transition heat was done with an In standard. The glass-transition temperatures (T_g's) were calculated with the half-step method, and the crystallinity was calculated with the value of 207 J/g for 100% crystalline PP.[20]

Wide-angle X-ray scattering (WAXS)

The WAXS measurements were obtained with a four-circle diffractometer (P4) with a HiStar/GADDS area detection system (Bruker AXS GmbH, Karlsruhe, Germany) with Cu Kα radiation.
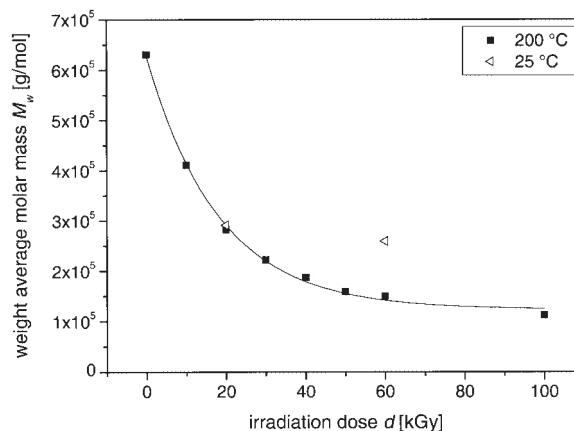

Figure 2   Weight-average molecular weight versus the irradiation dose for the initial iPP and irradiated samples at 200 and 25°C.

Rheological measurements

The elongational flow experiments presented in this study were performed with an oil-bath extensional rheometer. This device was self-constructed at the Institute of Polymer Materials of University Erlangen–Nürnberg and was described in detail by Münstedt and coworkers.[21,22] For measuring the elongational viscosity, a cylindrical sample was stretched vertically in a silicone oil bath. Constant strain rate experiments at a constant temperature of 180°C were run with different elongational rates between 0.01 and 0.3 s^{-1}.

The tensile stress growth coefficient or elongational viscosity [$\eta_E^+(t,\dot{\varepsilon}_0)$] was obtained from the measured tensile stress [$\sigma(t,\dot{\varepsilon}_0)$] divided by the applied constant strain rate ($\dot{\varepsilon}_0$):

$$\eta_E^+(t,\dot{\varepsilon}_0) = \sigma(t,\dot{\varepsilon}_0)/\dot{\varepsilon}_0 \qquad (3)$$

RESULTS AND DISCUSSION

SEC

The molecular characterization of PP included the investigation of the molar masses and radii of gyration. The weight-average molar mass as a function of the irradiation dose is plotted in Figure 2. As expected, molar mass degradation takes place subject to the irradiation dose. This is also illustrated by the differential molar mass distribution of samples irradiated at 200°C in Figure 3. High-molar-mass degradation takes place, especially in the high-molar-mass amounts. The irradiation at 200°C leads to higher molar mass degradation in comparison with the irradiation at 25°C. This is observed especially at higher irradiation doses. It is assumed that the thermal degradation plays an important role by the irradiation in the molten state.

Another question is the formation of chain branching. Therefore, the dependence of $\langle s^2 \rangle$ on the molar
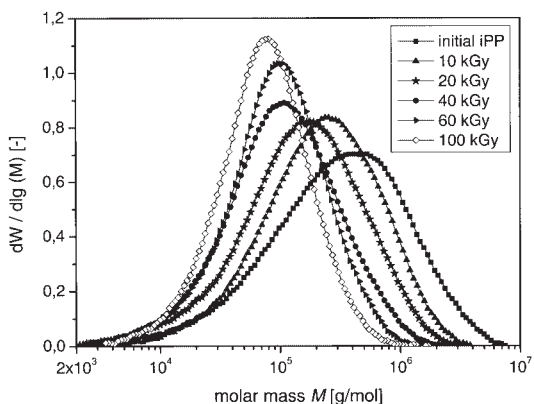
Figure 3 Differential molar mass distribution for the initial iPP and irradiated samples at 200°C.

Figure 5 Overlay of $\langle s^2 \rangle$ and the differential molar mass distribution versus the molar mass for different irradiated samples with 40 and 100 kGy at 200°C.

mass for the initial iPP and different irradiated samples is shown in Figure 4. $\langle s^2 \rangle$ for macromolecules at the same molar mass significantly decreases for these samples. This deviation of $\langle s^2 \rangle$ is an indication of increasing coil density with increasing irradiation dose, which can be related to the formation of LCB.

Additional, a comparison of the degree of branching for the irradiation at 25 and 200°C is illustrated in Figure 4. In the case of 20 kGy, the irradiation at 200°C leads to a higher decrease in the radius of gyration in comparison with the irradiation at 25°C. Furthermore, the radius of gyration for the sample irradiated at 60 kGy (25°C) is higher than the radius of the sample irradiated at 20 kGy (200°C). Irradiation in the molten state generally generates a lower radius of gyration or a higher degree of branching than irradiation in the solid state at the same irradiation dose. That means that irradiation in the molten state is more effective with respect to the formation of LCB.

For the samples irradiated at 200°C with a dose higher than 40 kGy, this interpretation with respect to LCB is not possible. An overlay of the mean-square
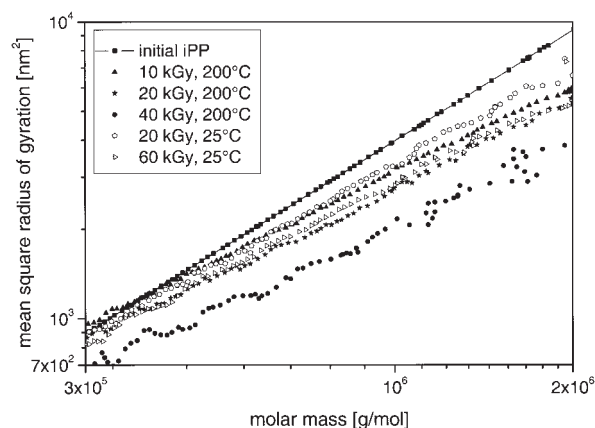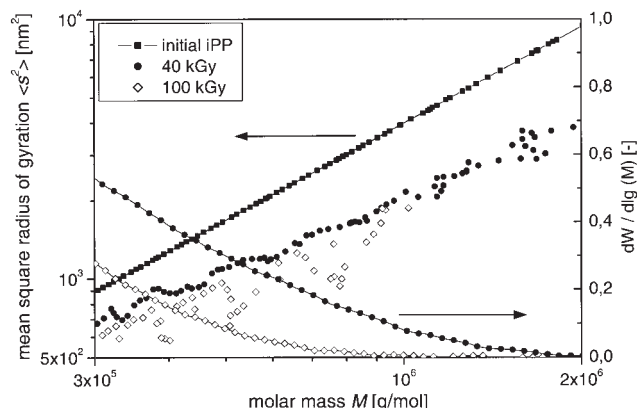
radii of gyration and differential molar mass distributions versus the molar mass is shown in Figure 5. With the irradiation dose increasing up to 100 kGy, a significant molar mass degradation can be observed. The concentration of high-molar-mass molecules is reduced, and this is followed by a very strong scattering of calculated radii. The deviation of $\langle s^2 \rangle$ and the molar mass in high-molar-mass areas can be explained on the one hand by the limitations of the calculation method used in the applied commercial software. On the other hand, at the beginning of the chromatographic separation, the concentrations of the polymer solutions are presumably not sufficiently high for a correct interpretation of their light scattering properties and the calculation of their molar masses and $\langle s^2 \rangle$ values. Therefore, a quantitative statement of LCB is not made for samples irradiated at doses higher than 40 kGy. However, in comparison with irradiation at room temperature,[7] increasing LCB is assumed. The knowledge of the interplay of both competitive processes, the formation of LCB and molar mass degra-
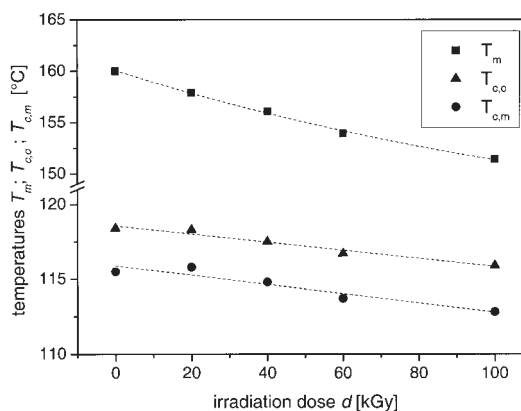

Figure 4 $\langle s^2 \rangle$ versus the molar mass for the initial iPP and irradiated samples up to 40 kGy at 200 and 25°C.

Figure 6 T_m, $T_{c,m}$, and $T_{c,o}$ versus the irradiation dose for the initial iPP and irradiated samples at 200°C.

TABLE I
DSC Data for the Cooling Run and Second Heating Run of PP Films with Respect to Irradiation Dose

Irradiation dose (kGy)	T_g (°C)	Melting enthalpy (J/g)	Crystallinity (%)	T_m (°C)	$T_{c,m}$ (°C)	$T_{c,o}$ (°C)
0	−7.7	100.9	49	160.0	115.5	118.4
20	−7.6	103.8	50	157.9	115.8	118.3
40	−8.5	104.3	50	156.1	114.8	117.5
60	−9.1	103.7	50	153.9	113.7	116.7
100	−11.0	101.6	49	151.4	112.8	115.9

dation, is the key to successful modification with respect to LCB. With an increasing irradiation dose in the molten state, the chain branching becomes more and more important. The degree of branching is higher than irradiation in the solid state. No changes in the molar mass and radius of gyration are found if PP is heated to the molten state without irradiation.[23]

DSC

The characteristic temperatures of melting and crystallization were determined with the peak temperatures [melting peak temperature (*s*) and maximum crystallization temperature ($T_{c,m}$)] and the extrapolated onset temperature of the crystallization ($T_{c,o}$; see Fig. 6). T_g's were calculated from the second heating run.

The irradiation results in LCB and molar mass degradation. The thermal behavior of LCB in PP is excepted to be comparable to that of the linear main chain because of the ability to crystallize. The overall crystallinity in the irradiated PP films is about 50% and independent of the dose (see Table I). The second process of degradation causes a change in the transition temperatures. T_m and $T_{c,m}$ as well as $T_{c,o}$ decrease with an increasing dose (see Fig. 6). The temperature difference between $T_{c,o}$ and $T_{c,m}$ as a measure of the crystallization rate is unchanged. Although T_g only

varies by 4 K, the tendency is clear: the higher the does, the lower T_g.

Another aspect is the shape of the melting peak. With an increasing dose, multiple melting peaks are observed in the DSC curves. From WAXS experiments, the formation of β modification could be excluded (see Fig. 7). The origin of this behavior should be melting and reorganization during heating. This phenomenon has already been discussed for a long time. The difficulty is the high recrystallization rate of the material. That means high heating rates are necessary to prevent reorganization during heating. Minakov et al.[24] investigated this process in poly(ethylene terephthalate), using a combination of results from a common differential scanning calorimeter, a hyper differential scanning calorimeter, and a chip calorimeter to reach high heating rates. In Figure 8, the second heating runs of PP irradiated with 100 kGy as examples are plotted. For comparison, the normalized heat flow is related to the heating rate. The lower T_m shifts as expected to higher values with an increasing heating rate. The higher T_m as a result of the reorganization shifts to lower values and is diminished at 80 K/min.

Rheology

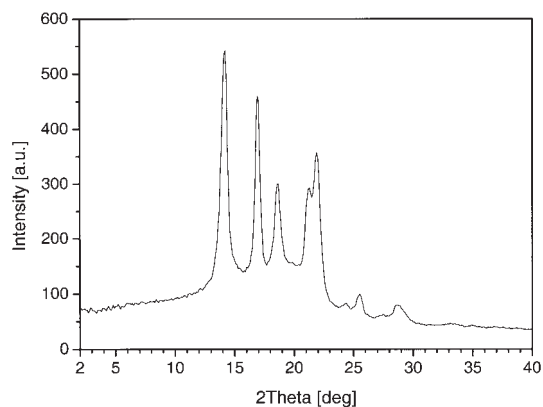Elongational flow experiments are a sensitive tool for the investigation of LCB, too. The occurrence of strain

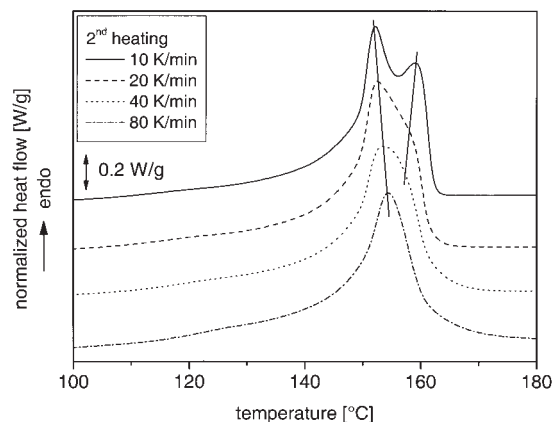**Figure 7** WAXS curves of a sample irradiated with 100 kGy at 200°C.

Figure 8 Melting (second heating) versus the heating rate for samples irradiated with 100 kGy at 200°C.
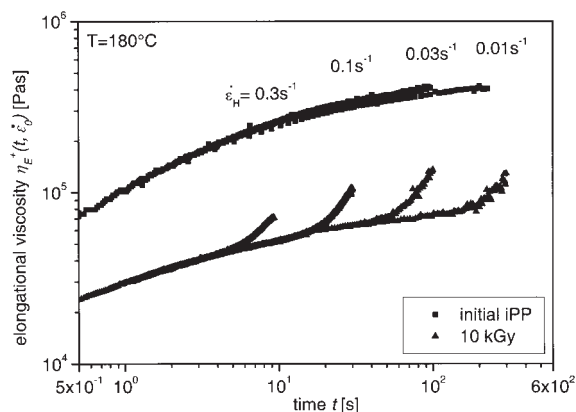
Figure 9 Elongational viscosity $[\eta_E^+(t)]$ versus the time (t) and different Hencky strain rates ($\dot{\varepsilon}_H$) at 180°C for the initial iPP and a sample irradiated with 10 kGy at 200°C.

hardening is related to LCB, if other reasons such as high-molar-mass components or a very broad molar mass distribution can be excluded. For linear PPs, no strain hardening is reported in the literature, and this has been observed for the untreated iPP, too (Fig. 9). The samples irradiated with 10 kGy at 200°C show strain hardening, which increases at lower strain rates (see Fig. 9). The strain rate dependence of randomly branched polyolefins is characteristic for different molecular structures.[25] This behavior is typically found for polyethylene[25–27] and PP[8] with a small amount of LCB.

CONCLUSIONS

The electron-beam irradiation of PP in the molten state is an additional way of creating LCB without additives. In the results of chromatographic measurements, a deviation of $\langle s^2 \rangle$ between initial and irradiated samples could be detected. The rheological measurements in elongation flow have confirmed the presence of LCB. With an increasing irradiation dose, different effects have been observed. As expected, high-molar-mass degradation takes place. Samples irradiated at 200°C have lower molecular weights than samples irradiated at 25°C. The degree of LCB is increased. A comparison of the modifications in the molten state and in the solid state leads to the conclusion that irradiation at 200°C generates higher branched samples. Additionally, DSC measurements show that a reduction of T_m, $T_{c,m}$, $T_{c,o}$, and T_g occurs.

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