

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/259662882>

Long-Chain Branched Polypropylenes by Electron Beam Irradiation and Their Rheological Properties

ARTICLE *in* MACROMOLECULES · DECEMBER 2004

Impact Factor: 5.8 · DOI: 10.1021/ma030579w

CITATIONS

164

READS

129

8 AUTHORS, INCLUDING:



Dietmar Auhl

Maastricht University

48 PUBLICATIONS 752 CITATIONS

SEE PROFILE



Beate Krause

Leibniz Institute of Polymer Research Dresden

42 PUBLICATIONS 1,190 CITATIONS

SEE PROFILE



Alben Lederer

Leibniz Institute of Polymer Research Dresden

81 PUBLICATIONS 1,171 CITATIONS

SEE PROFILE

Long-Chain Branched Polypropylenes by Electron Beam Irradiation and Their Rheological Properties

Dietmar Auhl, Jens Stange, and Helmut Münstedt*

University Erlangen-Nürnberg, Institute of Polymer Materials, Martensstr. 7,
D-91058 Erlangen, Germany

Beate Krause, Dieter Voigt, Albena Lederer, Uwe Lappan, and Klaus Lunkwitz

Leibniz-Institute of Polymer Research Dresden, Hohe Str. 6, D-01069 Dresden, Germany

Received December 8, 2003

ABSTRACT: The aim of this paper is to investigate how the molecular structure of linear polypropylenes can be modified by electron beam irradiation. For this purpose a linear precursor was irradiated with different doses. The samples were analyzed by size-exclusion chromatography coupled with a light scattering detector. With increasing doses, a reduction of molar mass and an increasing number of long-chain branches were found. Moreover, conclusions with respect to the topography of the long-chain branches obtained were drawn from the molar mass dependence of the zero shear viscosity of the irradiated samples, which deviates significantly from that of linear polypropylenes. The experimental results can be interpreted in a way that at low doses very few but long branches occur. At higher doses more and shorter branches per molecule exist. The elongational experiments clearly exhibit a change of the strain-hardening behavior with irradiation dose, which is in agreement with the structural changes concluded from the shear measurements. The results from rheology and their interpretation demonstrate two features. First, rheological experiments conducted on irradiated polypropylenes are much more sensitive with respect to long-chain branching than the classical characterization methods based on size-exclusion chromatography coupled with light scattering. Second, from a comparison of the rheological behavior of linear and irradiated polypropylenes some conclusions can be drawn regarding the topography of the long-chain branches generated.

Introduction

Isotactic polypropylene (iPP) is a fast growing commodity resin since it has many desirable and beneficial physical properties such as high stiffness, resistance to corrosive chemicals, and low specific gravity. Rheological properties of the melt are strongly affected by molar mass, molar mass distribution, and the presence of long-chain branching (LCB). Long-chain branched polypropylenes possess advantageous properties, which are important in many industrial applications, e.g., good thermoforming behavior, high melt strength, and uniform fine cell structure of extruded foams.^{1,2} Therefore, different methods have been applied in the past to modify polypropylenes by long-chain branches. One way to achieve this goal is electron beam irradiation. Widely unknown, however, is the molecular structure and particularly the topography of the long-chain branches generated by irradiation. Rheological properties react very sensitively on molecular changes, and from measurements on rather well-defined long-chain branched polystyrenes,³ polyisoprenes,⁴ and polyethylenes^{5–7} some results were obtained, which allow some insight into relationships between rheology and the topography of LCB. That is the reason why besides classical methods rheological investigations were used to characterize the polypropylene samples irradiated with various doses.

Some contributions to a deeper theoretical understanding of the effect of LCB have been made from the theoretical side by several authors. They were able to explain, for instance, the empirically found exponential dependence of the zero shear viscosity η_0 for star

polymers on the ratio of M_a/M_e .^{8,9}

$$\eta_0 \propto \left(\frac{M_a}{M_e}\right)^\alpha \exp\left(\nu \frac{M_a}{M_e}\right) \quad (1)$$

The molar mass M_e of a strand between two entanglements is a characteristic parameter of a polymer, M_a describes the molar mass of the long-chain branch, and α and ν are constants of the order of 1 and 0.5, respectively.

Materials and Methods

The isotactic polypropylene (iPP) homopolymer used in this study was the commercial product Novolen PP H2150 from Basell Polyolefins. 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/cm³. The peak melting temperature of the polypropylene was found as 163 °C.

Sample Preparation. Long-chain branches in polypropylene can be formed by after-treatment of a linear precursor, e.g., by reactive extrusion^{10,11} or radiation modification.^{12,13} It is well-known that the interaction of electrons with polymeric materials produces free radicals, which can react in several ways.¹⁴ A procedure to modify the molecular structure of an initially linear polypropylene by electron beam irradiation was described by DeNicola¹⁵ and Scheve et al.^{16,17} The main molecular effects are chain scission, chain branching, and cross-linking. Usually, all these reactions take place simultaneously and depend on different parameters, such as the chemical structure and the morphology of the polymer as well as the irradiation conditions including after-treatment.¹⁸ Reactions induced by scission and addition can be used to alter the molecular structure of the polymer. The final molecular structure of the modified polypropylene is mainly determined by the concentration of radicals, which are formed initially

* Corresponding author: polymer@ww.uni-erlangen.de.

during the irradiation process. Their number depends on the irradiation conditions and the total dose.¹⁴ The increase of the total dose leads to an enhancement of the concentration of free radicals, which form double bonds through β -scission and termination reactions. This makes the formation of branches more probable. Following from that, the electron beam irradiation of polypropylene without cross-linking agents has two effects on the molecular structure, namely the reduction of the molar mass and the formation of branches.^{12,18,19}

The iPP pellets were irradiated with 1.5 MeV electrons using an electron beam accelerator of the type ELV-2 (Budker Institute of Nuclear Physics, Russia) as described in detail by Dorschner et al.²⁰ The irradiation was carried out under a nitrogen atmosphere at atmospheric pressure in a special vessel.²¹ The sample was placed onto a support in this vessel, which includes heating elements and temperature sensors for temperature control. Before the vessel was filled with nitrogen it was evacuated to 10^{-2} Pa in order to minimize the concentration of oxygen. The sample was irradiated with different total doses d up to 150 kGy. Total doses d higher than 10 kGy were accomplished on a step-by-step basis with a dose of 10 kGy per pass in order to minimize the temperature increase, which results from the irradiation. After the irradiation process, the polypropylene was annealed for 30 min at 80 °C for a sufficient migration of chain fragments to free radicals to form chain branches. In the last step the deactivation of the residual radicals was realized by annealing for 60 min at 130 °C. The two annealing steps were carried out in the vessel under a nitrogen atmosphere, too.

After these modifications the surface of the polypropylene pellets was powdered with a mixture of two sterically hindered phenolic antioxidants (0.2% Irganox 1010 and 0.2% Irganox 245) and one organophosphite stabilizer (0.2% Irgafos 38). These heat stabilizers were applied in order to prevent the samples from thermooxidative degradation during sample preparation and rheological measurements.

Molecular Characterization. Molecular data were measured by high-temperature size-exclusion chromatography (SEC) coupled with a multiangle laser light scattering (MALLS) detector and a refractive index (RI) detector. The polymer molecules are fractionated in the SEC by their hydrodynamic volume, which depends on the density in the dissolved state, the molar mass, and long-chain branching. Therefore, the conventional SEC using linear polymer standards for the calibration is not suitable for investigations of the molar mass of branched polymer structures due to the fact that the calculated molar mass averages would be lower than the true values. By coupling SEC with MALLS, the absolute molar mass M_{LS} and the radius of gyration $\langle s^2 \rangle^{1/2}$ of every fraction can be determined directly. The ratio of the mean-square radius of gyration of a branched polymer $\langle s^2 \rangle_{br}$ to that of a linear polymer $\langle s^2 \rangle_{lin}$ is the so-called Zimm–Stockmayer branching parameter g .²²

$$g = \frac{\langle s^2 \rangle_{br}}{\langle s^2 \rangle_{lin}} \quad (2)$$

For the irradiated isotactic polypropylene a trifunctional randomly branched architecture can be assumed because a formation of branching points with a higher functionality is not probable for statistical reasons.²³ For such a trifunctional randomly branched polymer, g can be related to branching by

$$g = \left[\left(1 + \frac{m}{7} \right)^{0.5} + \frac{4m}{9\pi} \right]^{-0.5} \quad (3)$$

with m as the number of branching points along the molecule.²² From that the number of long-chain branches per 1000 monomer units λ is determined as

$$\lambda = \frac{m}{M} \times 1000 \times M_M \quad (4)$$

where M_M is the molar mass of the monomer unit and M is the molar mass of the branched polymer.

The SEC experiments were carried out using the apparatus PL-GPC 220 (Polymer Laboratories) at 150 °C coupled with a MALLS (DAWN EOS, Wyatt Technology) and a RI detector. The column set consists of two columns PL Mixed-B-LS (Polymer Laboratories). The eluent was TCB (1,2,4-trichlorobenzene, Merck) stabilized with diphenylamine (Merck). The software used for data processing and for calculation of the number of LCB was CORONA V1.40 for Windows (Wyatt Technology).

Rheological Characterization in Shear Flow. The rheological measurements in shear were performed at a temperature of 180 °C under a nitrogen atmosphere using a rotational rheometer with a plate–plate geometry of 25 mm in diameter and a gap of 1.5 mm. Cylindrical samples of a thickness of 2 mm and a diameter of 25 mm were prepared from the irradiated and stabilized pellets in a hot press at a temperature of 180 °C. An ARES instrument (Advanced Rheometric Expansion System) manufactured by Rheometric Scientific was used for stressing and dynamic-mechanical experiments. Shear creep measurements were conducted with a constant stress rheometer (Bohlin CS-Melt). The applied constant shear stresses τ_0 were on the order of 10 Pa, i.e., in the linear range of deformation. In the steady state of deformation and at sufficiently long creep times the steady-state elastic part of the creep compliance in the linear range J_e^0 becomes very small compared to t/η_0 , and the creep compliance approaches the relation $J(t) \approx t/\eta_0$. The zero shear viscosity can be determined then according to

$$\lim_{t \rightarrow \infty} \frac{t}{J(t)} = \eta_0 \quad (5)$$

Rheological Characterization in Uniaxial Elongation Flow. The elongational experiments were carried out with an uniaxial extensional rheometer of the design by Münstedt, which has been described in detail by Münstedt et al.²⁴ and Kurzbeck et al.²⁵ A cylindrical sample is stretched vertically in a silicone oil bath, the density of which matches the density of the molten polypropylene as closely as possible. Constant strain rate experiments at a constant temperature of 180 °C were run with different elongational rates $\dot{\epsilon}_0$. The tensile stress growth coefficient or transient elongational viscosity is defined as $\eta_E^+(t, \dot{\epsilon}_0) = \sigma(t, \dot{\epsilon}_0)/\dot{\epsilon}_0$. The nonlinear behavior at which the tensile stress coefficient rises above the linear viscoelastic start-up curve given by 3 times the shear stress growth coefficient is called strain hardening. This behavior is very sensitive to the molecular structure and closely related to processing properties.^{1,26–28} The so-called strain-hardening factor X_E is determined by

$$X_E(t) = \frac{\eta_E^+(t, \dot{\epsilon}_0)}{3\eta_0^+(t)} \quad (6)$$

where $\eta_0^+(t)$ is the time-dependent shear viscosity in the linear range of deformation.

Results and Discussion

Molecular Characterization. The molar mass distributions of the samples irradiated with total doses from 2 up to 150 kGy are plotted in Figure 1. As expected, the molar masses decrease with increasing total doses. The irradiated samples have a reduced amount of high molar mass molecules compared to the initial polypropylene. The polydispersity factor M_w/M_n is slightly reduced by irradiation (Table 1). This fact leads to the conclusion that the degradation process becomes predominant in the high molar mass area of the polymer. A significant reduction of the molar mass M_w of the irradiated polymer was observed even at total doses lower than 20 kGy (Figure 2). Above a dose of 60

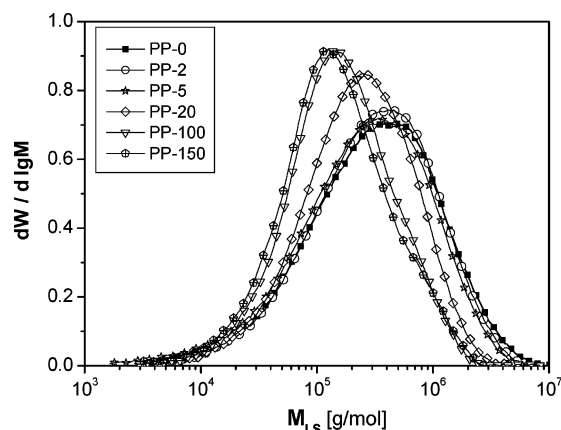


Figure 1. Molar mass distributions $dW/d \lg M$ for the initial iPP and irradiated samples. The numbers behind PP describe the irradiation doses in kGy.

Table 1. Molecular Characteristics of the Polypropylenes Investigated

sample	d [kGy]	M_n [kg/ mol]	M_w [kg/ mol]	M_w/M_n	λ	η_0 at 180 °C [kPa s]
PP-0	0	160	669	4.2		188
PP-1	1	148	563	3.8	n.d. ^a	196
PP-2	2	157	565	3.6	n.d.	221 ^b
PP-5	5	126	473	3.8	n.d.	236 ^b
PP-10	10	122	444	3.7	0.08	203
PP-20	20	128	384	3.0	0.14	107
PP-60	60	74	285	3.8	0.44	16
PP-100	100	83	279	3.4	0.53	4.8
PP-150	150	77	268	3.5	0.78	3.7

^a n.d.: not detectable. ^b The value of η_0 is even higher because the steady state is not yet reached in the experiments.

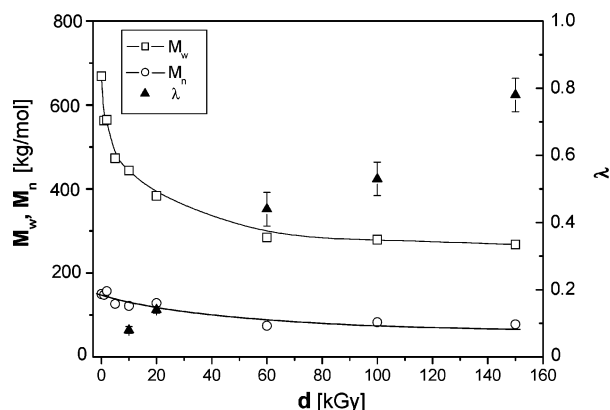


Figure 2. Molar mass averages M_w and M_n and numbers of LCB per 1000 monomers λ vs the irradiation dose d for the initial iPP and irradiated samples.

kGy the molar mass M_w seems to reach a nearly constant value. This result indicates a change in the effectiveness of the two competitive processes, i.e., degradation and branching. The branching, which causes an increase of the molar mass, becomes more and more important with higher doses.

The dependence of the root-mean-square radius of gyration on the molar mass for the initial PP and some of the samples irradiated with different doses is shown in Figure 3. The slope of 0.6 determined for linear PP is found to be higher than the theoretical value of 0.5 for theta solution since the temperature and solvent used for the experiments do not provide theta conditions. A reduction of the radius of gyration is found with irradiation, which depends on the total dose for mol-

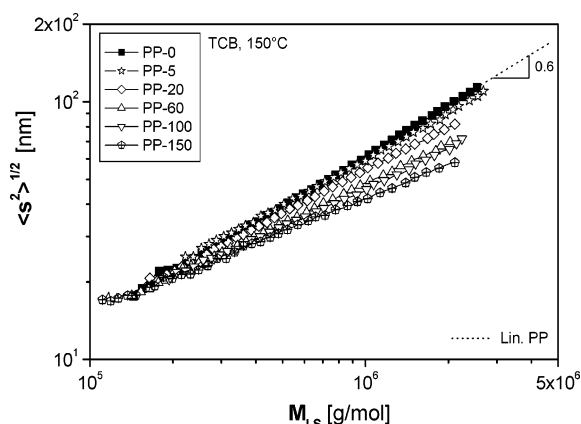


Figure 3. Root-mean-square radius of gyration $\langle s^2 \rangle^{1/2}$ vs the molar mass M_{LS} determined by light scattering for the initial iPP and the irradiated samples.

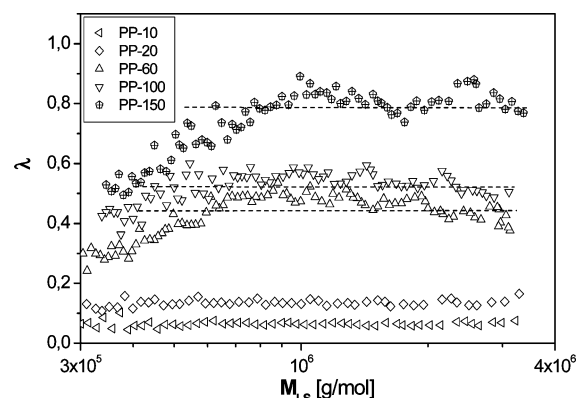


Figure 4. Number of LCB per 1000 monomers λ vs the molar mass M_{LS} determined by light scattering for the samples irradiated with different doses.

ecules of the same molar mass. A distinct deviation of the radius of gyration from that of the linear PP can only be observed for the samples irradiated with doses of 10 kGy and higher. That means for the samples irradiated with doses of 5 kGy and lower the question cannot be answered from light scattering measurements whether there exist long-chain branches induced by irradiation or not. The numbers of LCB per 1000 monomers λ are calculated according to eqs 3 and 4, and they were found to be nearly constant for each sample in the range between 5×10^5 and 3×10^6 g/mol (Figure 4). The value of λ increases with the applied total dose, and therefore, it can be concluded that a growing concentration of primary radicals leads to a more pronounced formation of branches (cf. Figure 2). The dependence of λ on the dose d is found to be approximately linear in the range measured. Although the calculation of this number is based on several assumptions, it shows that the degree of branching is relatively low. For the sample irradiated with 10 kGy, which consists of about 3000 monomer units, the analysis results in about 0.3 long-chain branches per molecule, whereas for PP-150, which consists of about 2000 monomer units, the calculated value is about 1.5 long-chain branches. This simple estimation of the average number of branches demonstrates that a mixture of branched and linear molecules is highly probable up to medium doses and that the samples irradiated with high doses contain molecules with more than one long-chain branch.

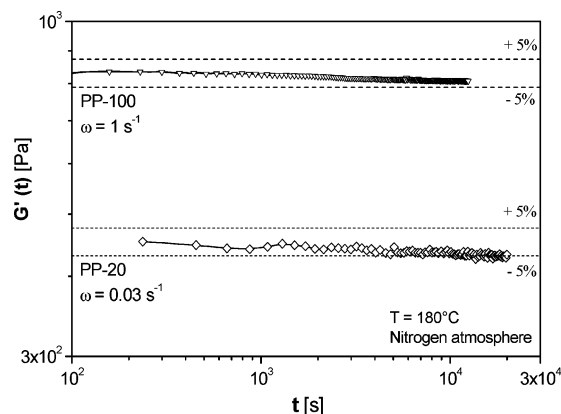


Figure 5. Determination of the thermal stability by measuring the storage modulus G' as a function of time at 180°C for PP-20 and PP-100 (nitrogen atmosphere).

Rheological Characterization of the Thermal Stability. To avoid a misinterpretation of rheological measurements, it is important to ensure that the molecular structure does not change during the experiment. Dynamic-mechanical measurements at low frequencies are a sensitive tool for probing the thermal stability of polymer materials. Tests with regard to the thermal stability were carried out by time sweeps at sufficiently low angular frequencies. As an example, the samples irradiated with 20 and 100 kGy are shown in Figure 5. The time at which the modulus has fallen by 5%—this value is arbitrarily assumed as the stability limit—is at least 10^4 s. This time is long enough to grant a sufficient thermal stability for the different kinds of rheological experiments performed.

Oscillatory Shear Flow Measurements. The complex dynamic shear viscosity $\eta^*(\omega)$ was measured over a range of 4 decades of the angular frequency ω at a temperature of 180°C . Figure 6a clearly shows a decreasing viscosity with higher irradiation doses, which means the viscosity is dominated by the molar mass reduction. The complex viscosity is shown as a reduced plot (Figure 6b) in order to assess the shear-thinning behavior, which is an important issue from the practical point of view. The zero shear viscosities used for the reduced plots were obtained from the creep experiments as presented in Figure 8.

The shear-thinning behavior is found to change slightly for the weakly irradiated samples PP-1 and PP-2, but it does not change any further with the dose and is similar for all other irradiated samples. Nevertheless, a somewhat broader transition zone between the Newtonian behavior and the power-law flow region is observed for the branched polypropylenes, which is typical of long-chain branched polymers, e.g., star polystyrenes.³ In the latter paper it was shown that long-chain branching increased the shear-thinning behavior. As the polydispersity factors M_w/M_n of the polypropylenes investigated do not change very much by the irradiation (Table 1), it can be concluded that the introduced branching has no pronounced effect on the shear-thinning behavior.

Recently, a plot of the phase angle δ vs the complex shear modulus $|G^*(\omega)|$ is frequently used to get an insight into long-chain branching.²⁹ This plot is applied to the irradiated samples (Figure 7). In the medium range of the complex modulus between the rubbery plateau region and the Newtonian region a significant deviation of the phase angle δ beneath the curve of the

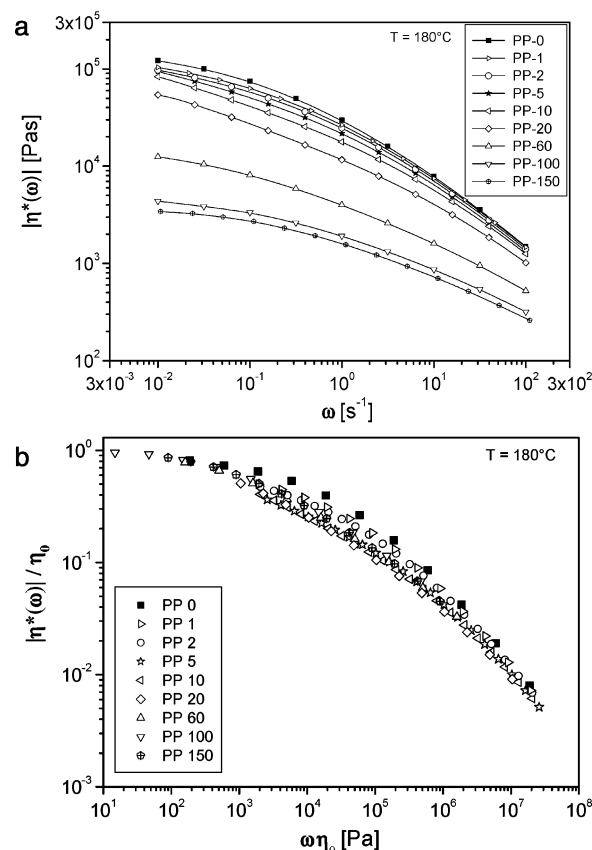


Figure 6. Dynamic-mechanical measurements on the various polypropylenes. (a) Complex shear viscosity $|\eta^*(\omega)|$ as a function of the angular frequency ω . (b) Reduced plot at 180°C .

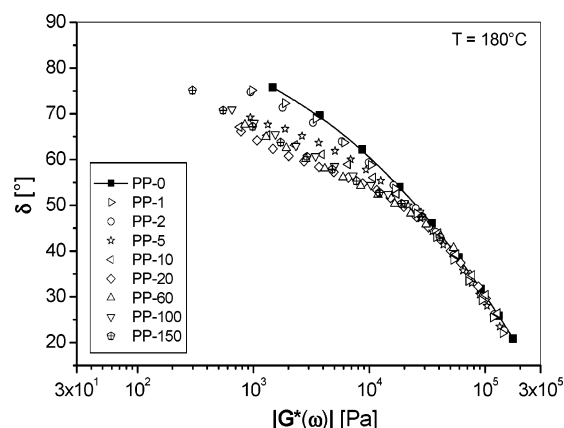


Figure 7. Phase angle δ as a function of the complex shear modulus $|G^*(\omega)|$ at 180°C for all polypropylenes.

linear polypropylene is observed for the samples irradiated with 5 kGy and higher. Up to an irradiation dose of 20 kGy the phase angle decreases at small moduli and remains constant for higher ones within the accuracy of the measurements. A shift of the phase angle toward smaller values at fixed $|G^*(\omega)|$ can be caused by a broader molar mass distribution or an introduction of long-chain branching. For the irradiated polypropylenes the decrease can only be attributed to the introduction of long-chain branching since the polydispersity slightly decreases with irradiation. Therefore, these results indicate that the irradiated samples contain long-chain branches, but the observed deviation is not

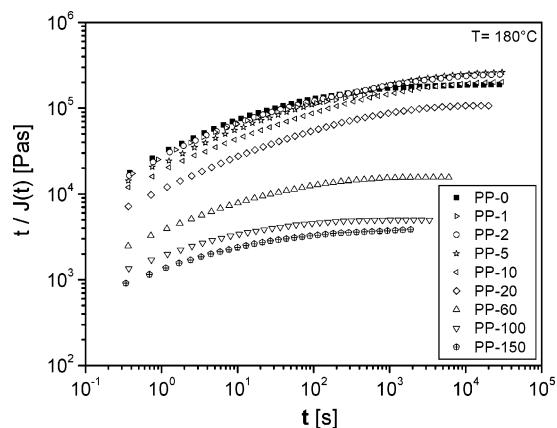


Figure 8. $t/J(t)$ as a function of creep time t at 180 °C for all polypropylenes.

very strong; hence, it is very difficult to distinguish between the samples.

Creep Measurements in Shear Flow. The zero shear viscosity as a function of M_w is a very sensitive quantity to detect even low amounts of long-chain branching.^{30,31} Creep tests are very suitable for the determination of the zero shear viscosity η_0 as the steady state is reached much faster than in stressing experiments. According to eq 5, the limiting value of the ratio of creep time t and shear creep compliance $J(t)$ at long creep times corresponds to the value of the zero shear viscosity. This ratio $t/J(t)$ is plotted as a function of the creep time t in Figure 8 for all samples investigated.

A slightly increased zero shear viscosity compared to the untreated polypropylene is observed for the samples irradiated with low doses of 2 and 5 kGy although M_w is lower (cf. Table 1). In contrast to these two doses, the value of PP-10 was found to be less than that of PP-5, indicating a viscosity maximum between 2 and 10 kGy. For the polypropylenes irradiated with more than 10 kGy a declining zero shear viscosity was observed. The data do not allow any conclusion with respect to the branching structure, however, as the molar mass has changed by the irradiation. But this influence can be taken into account if η_0 is plotted as a function of M_w and compared to the relationship of linear samples. Figure 9 shows the results. The relationship for the linear polypropylenes is very well described by $\log \eta_0 = -15.4 + 3.5 \log M_w$ as shown by the full line. This finding is in very good agreement with results from the literature.^{32,33} It was shown for several polymers that the polydispersity has no measurable influence on the relationship between zero shear viscosity and M_w , e.g., for polyethylene,³¹ for polypropylene,³² for polystyrene,³⁴ and for polybutadiene.³⁵ This fact is of great importance for a correlation between rheological properties and branching topographies, as it is well-known from literature that this power law does not hold for polymers with branched molecular structures.

Therefore, for the LCB-PP obtained by electron beam irradiation η_0 was plotted as a function of molar mass (cf. Figure 9). A significant rise above η_0 for a linear polypropylene of the same molar mass is observed in the case of polypropylenes irradiated with low doses up to 20 kGy while the samples irradiated with higher doses of 60–150 kGy approach again the line of linear polypropylenes at lower weight-average molar masses. For PP-100 and PP-150 the measured values come to

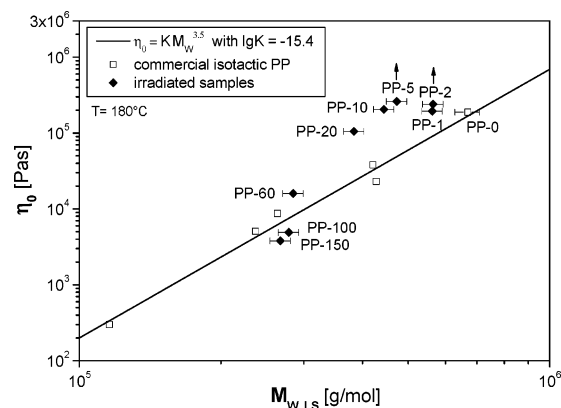


Figure 9. Weight-average molar mass M_w dependence of the zero shear viscosity η_0 at 180 °C (M_w determined from SEC-MALLS). The arrows indicate that the actual zero shear viscosity is higher than the plotted value because a steady state could not be obtained in the measurements. Confidence bars indicate an error of the molar mass of $\pm 5\%$. The units of K are $[\text{Pa s} (\text{g/mol})^{-3.5}]$.

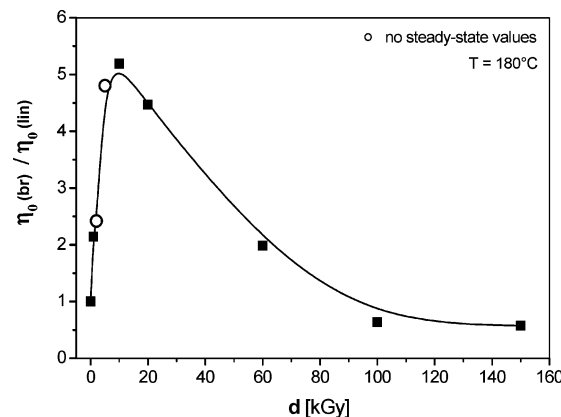


Figure 10. Ratios of the zero shear viscosities η_0 of branched and linear PP vs the irradiation dose d .

lie even below the line for the linear samples. Figure 10 gives a more quantitative picture of these relationships. It demonstrates that the viscosity ratio of the branched to the linear samples as a function of the irradiation dose steeply rises to a maximum, which reaches the value of 5 for a dose of 10 kGy. This finding indicates how sensitively the zero shear viscosity reacts on the electron beam irradiation. On the other hand, it demonstrates the analytical potential of viscosity measurements with respect to long-chain branching.

Gabriel and Münstedt³⁶ concluded from investigations on a number of polyethylenes that slightly long-chain branched PE with a starlike molecular structure come to lie above the line of linear PE whereas a position beneath the line indicates a treelike topography. This was explained by the exponential dependence of η_0 on the ratio of M_a/M_e (cf. eq 1). Taking these findings into account one can draw a conclusion with respect to the branching topography of the samples of Figure 9. Whereas for PP-1 to PP-60 a starlike shape is probable, a treelike topography becomes more likely for PP-100 and PP-150.

Uniaxial Elongational Flow Measurements. The tensile stress growth coefficients $\eta_E^+(t, \dot{\epsilon}_0)$ presented in Figure 11a,b are obtained from stressing experiments at constant Hencky strain rates. For each irradiation dose the respective curves superpose at all applied strain rates on the linear viscoelastic start-up curve up

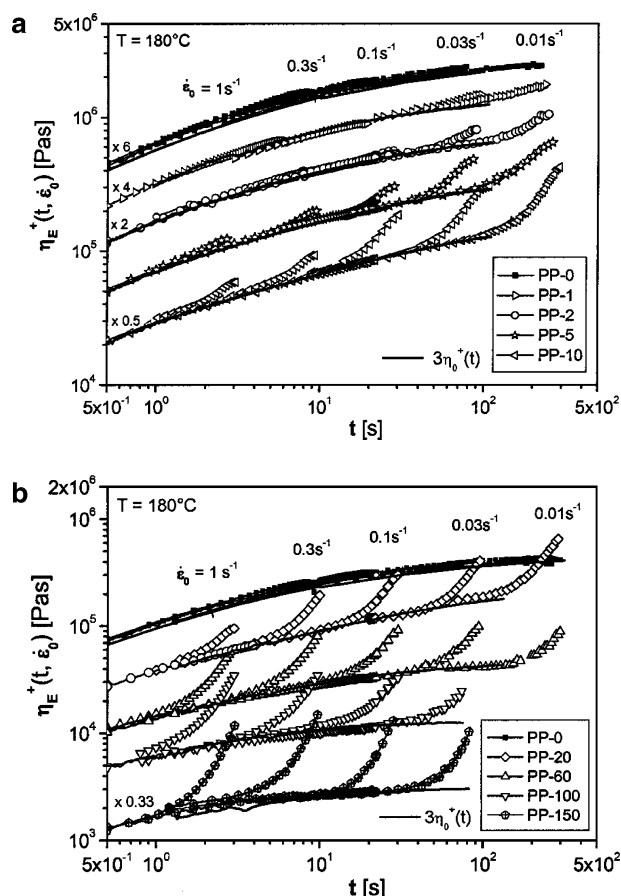


Figure 11. Tensile stress growth coefficient $\eta_E^+(t, \epsilon_0)$ as a function of time t at different Hencky strain rates ϵ_0 . (a) Initial iPP and the irradiated samples up to PP-10. (b) Initial iPP and the irradiated samples PP-20 up to PP-150.

to a Hencky strain of about 1. Trouton's law, which compares the shear and elongational viscosity in the linear range of deformation, is fulfilled for all samples and gives evidence of the reliability of the experiments.

For the polypropylene homopolymer the elongational flow experiments show that the tensile stress growth coefficient is 3 times the shear stress growth coefficient at all constant Hencky strain rates measured; i.e., no strain hardening is observed for the nonirradiated sample at Hencky strains smaller than 2.9 (Figure 11a). A behavior similar to the polypropylene homopolymer is found for the polypropylene irradiated with 1 kGy. But from Figure 11a,b it can be seen that all other irradiated samples show strain hardening. The amount of it becomes more pronounced at higher irradiation doses. Furthermore, the strain-rate dependence of the strain-hardening factor at $\epsilon_H = 2.7$ differs for the polypropylenes irradiated with various doses. This behavior is shown in Figure 12. For the samples irradiated with 2–20 kGy the strain-hardening factor decreases with increasing strain rates. This behavior is typically found for polyethylenes with a small amount of long-chain branching.^{36,37} In contrast to the weakly irradiated samples, the strain hardening for PP-60 is nearly independent of strain rate while for PP-100 and PP-150 it increases significantly with strain rate. The latter behavior is found for low-density polyethylene (LDPE) with a high amount of long-chain branching and a treelike molecular structure.^{36,37} From the differences of the strain-rate dependence of X_E ($\epsilon_H = 2.7$) it can be

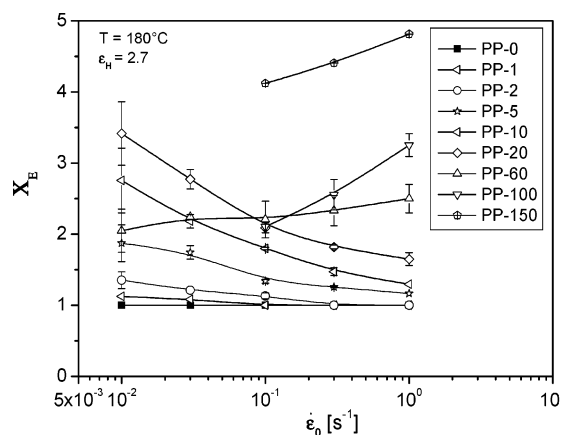


Figure 12. Strain-hardening factor X_E as a function of strain rate ϵ_0 at a Hencky strain of 2.7.

concluded that the branching structure is changed with irradiation dose.

To discuss the relationship between branching topographies and elongational properties, two effects have to be excluded. Polydispersity or high molar mass components can influence the elongational viscosity as it has been demonstrated e.g. for polystyrenes of different molar mass distributions.³⁸ Distinct amounts of high molar mass components caused a significant increase in strain hardening at high strain rates. For linear polypropylenes of different polydispersities no strain hardening was found, however.³⁹ For the irradiated polypropylenes the SEC-MALLS measurements show that the polydispersity is even decreasing with irradiation dose, and no high molar mass components are found. That means the results can be related to the branching structure. A second factor, which could in principle influence strain hardening, is a deformation-induced crystallization. This effect can be excluded as the experiments were carried out at 180 °C, i.e., well above the melting range. Moreover, no haze was observed during the elongation of the transparent samples.

The not irradiated polypropylene begins to neck in and to fail at $\epsilon_H = 2$. In contrast, some of the specimens of the weakly irradiated samples PP-1 to PP-5 can be stretched up to the final Hencky strain of 3, especially at low strain rates, and deform homogeneously until the end of the test. The specimens of the medium and highly irradiated PP-10 to PP-150 show a more homogeneous deformation at high Hencky strains compared to the weakly irradiated polypropylenes. They all can be elongated up to the final Hencky strain of 3. These observations can obviously be correlated with the amount of strain hardening. The homogeneity of the sample deformation is not only a precondition for reliable measurements but also an important issue from the practical point of view, since a homogeneous deformation behavior is desired in many processing operations with elongational flows, e.g., film blowing and thermoforming.

Conclusions

Long-chain branches can be introduced into linear polypropylenes by electron beam irradiation without cross-linking. An addition of special additives for branching is not necessary. It was found that an increase of the irradiation dose has two consequences. First, a reduction of molar mass takes place, and second, an increase of the number of long-chain branches occurs.

The samples investigated have to be assumed randomly branched since the length of the branches and their position on the polymer backbone are controlled by the statistical nature of the irradiation process.

The reduction of molar mass and the long-chain branching introduced show a significant influence on the viscoelastic properties of the melts. From oscillatory shear flow measurements a deviation of the $\delta-|G^*|$ curve from that of the linear polypropylene was found, which can be attributed to the presence of long-chain branching. A distinct correlation with the molecular structure was not obvious, however. A significant increase of the zero shear viscosities of the irradiated samples compared to those of untreated polypropylenes of the same weight-average molar mass was observed, which rises at a low amount of LCB to a maximum above the line of linear polypropylenes but approaches it again at higher LCB contents. This increase is explained by small amounts of long-chain branches with relatively long arms and hence a high ratio of M_a/M_e , which has an exponential influence on η_0 .

The decrease of $\eta_{0,br}/\eta_{0,lin}$ at higher doses can formally be related to a decline of the molar mass M_a of the branches. The reason for this change can be sought in two mechanisms. First, the molar mass decreases with irradiation dose, and following from that the length of the molecules attached to the backbone becomes shorter. Second, it is not unrealistic to assume that a change of architecture from starlike to treelike branches takes place with irradiation. A treelike structure is characterized by branches randomly distributed along the chains, resulting in a higher number of chains with smaller values of M_a than in the case of few long-chain branches.

The samples irradiated with more than 1 kGy show a distinct strain hardening in elongational flow with changing strain rate dependence. Two conclusions can be drawn from the results. First, it is clearly demonstrated that there is a strong relationship between strain hardening and branching. This can be concluded from the finding that strain hardening increases for the more strongly irradiated samples although the molar mass has become significantly lower, resulting in shorter relaxation times. The facts that the polydispersity remains nearly constant after irradiation of the polymer and a high molar mass component was not detectable mean that the elongational viscosity can be used as an indicator for the generation of long-chain branching in polypropylene by electron beam irradiation.

Second, from the rate dependence of strain hardening conclusions may be drawn with respect to the topography of the various polypropylene molecules. A decreasing strain hardening with increasing strain rate as was found for less irradiated samples points to a small degree of branching with high molar masses M_a of the branches. A strain hardening increasing with strain rate indicates a high degree of branching with small arm molar masses M_a as is typically found for LDPE. These conclusions concerning the topography of the long-chain branches in electron beam irradiated polypropylenes could be the experimental base for comparison with theories on radical reactions.

The results of this work also show that rheological results measured in shear and elongational flow are much more sensitive to the presence of long-chain branches than the quantities used in the analysis by size-exclusion chromatography. This finding means that the entanglement network reacts much more sensitively

to long-chain branching than the hydrodynamic volume. Especially the viscosity at small shear rates is sensitive enough to detect even low amounts of LCB and to provide a deeper insight into the altered molecular structure.

Summarizing, the results lead to the conclusion that the polypropylenes investigated consist of branched molecular structures with an increasing number of long-chain branches at higher irradiation dose. There is strong evidence that this increase leads to a change of the branching structure. The results are in agreement with previous findings on polyethylenes. Therefore, they broaden the experimental base on the relationship between the rheological behavior of polymer melts and their molecular structure, which can be used in two ways. First, the results strengthen the role of rheological measurements as an analytical tool, and second, they give some hint in which way polypropylene can be modified by electron beam irradiation. This insight is particularly valuable if one intends to tailor polypropylene for special applications.

Acknowledgment. Financial support from the German Research Foundation (DFG) (Grants MU1336/7 and LU451/11) is gratefully acknowledged.

Note Added after ASAP Publication

This article was released ASAP on November 11, 2004. Figures 4 and 11 have been revised. The correct version was posted on December 2, 2004.

References and Notes

- (1) Phillips, E. M.; McHugh, K. E.; Ogale, K.; Bradley, M. B. *Kunststoffe* **1992**, *82*, 671–676.
- (2) Park, C. B.; Cheung, L. K. *Polym. Eng. Sci.* **1997**, *37*, 1–10.
- (3) Graessley, W. W.; Roovers, J. *Macromolecules* **1979**, *12*, 959–965.
- (4) Fetters, L. J.; Kiss, A. D.; Pearson, D. S.; Quack, G. F.; Vitus, F. J. *Macromolecules* **1993**, *26*, 647–654.
- (5) Wood-Adams, P.; Dealy, J. M.; deGroot, A. W.; Redwine, O. D. *Macromolecules* **2000**, *33*, 7489–7499.
- (6) Gabriel, C.; Münstedt, H. *Rheol. Acta* **2002**, *41*, 232–244.
- (7) Lohse, D. J.; Milner, S. T.; Fetters, L. J.; Xenidou, M.; Hadjichristidis, N.; Mendelson, R. A.; Garcia-Franco, C. A.; Lyon, M. K. *Macromolecules* **2002**, *35*, 3066–3075.
- (8) Pearson, D. S.; Helfand, E. *Macromolecules* **1984**, *17*, 888–895.
- (9) McLeish, T. C. B.; Larson, R. G. *J. Rheol.* **1998**, *42*, 81–110.
- (10) DeNicola, A. J., Jr. US Patent 5 047 485, 1989.
- (11) Lagendijk, R.; Hogt, A. H.; Buijtenhuijs, A.; Gotsis, A. D. *Polymer* **2001**, *42*, 10035–10043.
- (12) Yoshii, F.; Makuuchi, K.; Kikukawa, S.; Tanaka, T.; Saitoh, J.; Koyama, K. *J. Appl. Polym. Sci.* **1996**, *60*, 617–623.
- (13) Schulze, D.; Trinkle, S.; Mülhaupt, R.; Friedrich, C. *Rheol. Acta* **2003**, *42*, 251–258.
- (14) Charlesby, A. *Atomic Radiation and Polymers*; Pergamon Press: Oxford, 1960.
- (15) DeNicola, A. J., Jr. Europ. Patent 0 351 866, 1989.
- (16) Scheve, B. J.; Mayfield, J. W.; DeNicola, A. J., Jr. Europ. Patent 0 190 889, 1986.
- (17) Scheve, B. J.; Mayfield, J. W.; DeNicola, A. J. US Patent 4 916 198, 1990.
- (18) Valenza, A.; Piccarolo, S.; Spadaro, G. *Polymer* **1999**, *40*, 835–841.
- (19) Rätzsch, M.; Bucka, H.; Hesse, A.; Reichelt, N.; Borsig, E. *Macromol. Symp.* **1998**, *129*, 53–77.
- (20) Dorschner, H.; Jenschke, W.; Lunkwitz, K. *Nucl. Instrum. Methods Phys. Res. B* **2000**, *161–163*, 1154–1158.
- (21) Körber, H.; Lappan, U.; Geissler, U.; Lunkwitz, K.; Hanke, R. German Patent 19 930 742, 2001.
- (22) Zimm, B. H.; Stockmayer, W. H. *J. Chem. Phys.* **1949**, *17*, 1301–1314.
- (23) Sugimoto, M.; Tanaka, T.; Masubuchi, Y.; Takimoto, J.; Koyama, K. *J. Appl. Polym. Sci.* **1999**, *73*, 1493–1500.

- (24) Münstedt, H.; Kurzbeck, S.; Egersdörfer, L. *Rheol. Acta* **1998**, *37*, 21–29.
- (25) Kurzbeck, S.; Oster, F.; Münstedt, H.; Nguyen, T. Q.; Gensler, R. *J. Rheol.* **1999**, *43*, 359–374.
- (26) Münstedt, H.; Laun, H. M. *Rheol. Acta* **1981**, *20*, 211.
- (27) Hingmann, R.; Marczinke, B. *J. Rheol.* **1994**, *38*, 573–587.
- (28) Wagner, M. H.; Bastian, H.; Hachmann, P.; Meissner, J.; Kurzbeck, S.; Münstedt, H.; Langouche, F. *Rheol. Acta* **2000**, *39*, 97–109.
- (29) Trinkle, S.; Walter, P.; Friedrich, C. *Rheol. Acta* **2002**, *41*, 103–113.
- (30) Janzen, J.; Colby, R. H. *J. Mol. Struct.* **1999**, *485–486*, 569–584.
- (31) Gabriel, C.; Münstedt, H. *Rheol. Acta* **2002**, *41*, 232–244.
- (32) Fleissner, M. *Makromol. Chem., Macromol. Symp.* **1992**, *61*, 324–341.
- (33) Eckstein, A.; Suhm, J.; Friedrich, C.; Maier, R.-D.; Sassmannshausen, J.; Mülhaupt, R. *Macromolecules* **1998**, *31*, 1335–1340.
- (34) Masuda, T.; Kitagawa, K.; Inoue, T.; Onogi, S. *Macromolecules* **1970**, *3*, 116–125.
- (35) Struglinski, M. J.; Graessley, W. W. *Macromolecules* **1985**, *18*, 2630–2643.
- (36) Gabriel, C.; Münstedt, H. *J. Rheol.* **2003**, *47*, 619–630.
- (37) Malmberg, A.; Gabriel, C.; Steffl, T.; Münstedt, H.; Löfgren, B. *Macromolecules* **2002**, *35*, 1038–1048.
- (38) Münstedt, H. *J. Rheol.* **1980**, *24*, 847–867.
- (39) Trzebiatkowski, T.; Wilski, H. *Rheol. Acta* **1985**, *24*, 582–587.

MA030579W