

Characterization of Electron Beam Irradiated Polypropylene: Influence of Irradiation Temperature on Molecular and Rheological Properties

Beate Krause,¹ Dieter Voigt,¹ Liane Häußler,¹ Dietmar Auhl,² Helmut Münstedt²

¹Leibniz Institute of Polymer Research Dresden, Hohe Str. 6, 01069 Dresden, Germany

²University Erlangen-Nürnberg, Institute of Polymer Materials, Martensstr. 7, 91058 Erlangen, Germany

Received 22 March 2005; accepted 24 June 2005

DOI 10.1002/app.23453

Published online 9 February 2006 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: The aim of the investigations was to analyze the influence of the temperature during the irradiation process of polypropylene on the molar mass, the formation of long chain branching and the final branching topology. A linear isotactic polypropylene homopolymer was modified by electron beam irradiation at different temperatures, with two irradiation doses to insert long chain branching. The samples were analyzed by size exclusion chromatography coupled with a multiangle laser light scattering detector, by differential scanning calorimetry, and by shear and elongational rheology. The shear and elongational flow behavior is

discussed in terms of the influence of molecular parameters and used to analyze the topology of the irradiated samples. With increasing temperature, a slight reduction of the molar mass, an increase of long chain branching and an increase of crystallization temperature were found. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 100: 2770–2780, 2006

Key words: poly(propylene) (PP); electron beam irradiation; differential scanning calorimetry (DSC); rheology; long chain branching

INTRODUCTION

Commercial linear isotactic polypropylene (iPP) has many desirable and beneficial physical properties such as high stiffness, good resistance to corrosive chemicals and low specific gravity. Long chain branched polypropylene (PP) has further advantageous properties, which are important in many industrial applications, e.g., high melt strength, good thermoforming behavior and uniform fine cell structure by foam extrusion.^{1,2}

Electron beam induced reactions in PP and preparation of long chain branching

The molecular structure of linear PP can be significantly modified by electron beam irradiation. The main reactions during the irradiation process are chain scission, chain branching, and crosslinking. Usually all these reactions coexist. The effect, which predominates, is dependent on several factors, such as chemical structure and morphology of the polymer as well as the irradiation conditions and posttreatment.^{3–6}

In PP, the dominant reactions after formation of free radicals are first β -scission, with molar mass decrease

and formation of double bonds. Furthermore, the addition of free radicals to the double bonds takes place with forming chain branching followed by increasing of molar mass. Additionally, disproportionation or recombination reactions of two polymer radicals occur followed by changed molar masses.^{4–8} Therefore, the electron beam irradiation has two effects on the molecular structure: reduction of the molar mass and formation of chain branching.^{9,10}

In different patents^{11–14} the irradiation by electron beam under oxygen-free or reduced active oxygen atmosphere to form branched PP is described. This is achieved by using vacuum or by replacing the air by inert gas, i.e., nitrogen. Furthermore, the temperature of the polymer material should be kept at less than 40°C because an additional increase of the temperature in the material takes place during the irradiation. The dose of electron beam irradiation should be about 10–90 kGy. After the irradiation, the material should be annealed in two steps. The first annealing step at 40–120°C is necessary for a sufficient migration of chain fragments to free radicals to form chain branches. The second annealing step at a temperature of at least 120°C is sufficient to allow deactivation of substantially all residual free radicals.^{9,15} The radical reactions, which are necessary for forming branches, take place in the bulk and are presumably diffusion limited. It can be expected that higher temperatures are a requirement for a sufficient migration of chain fragments to free radicals to form chain branches.¹²

Correspondence to: D. Voigt (voigt@ipfdd.de).

The irradiation of PP can also be carried out at increased temperatures.^{16,17} A continuous method for producing PP powder mixtures of increased stress crack resistance and melt strength using low energy radiation is described in a patent.¹⁶ The samples are irradiated between 20 and 150°C under inert conditions. Another patent¹⁷ shows a process to crosslink PP-polyethylene-blends using low energy radiation. It was found that a temperature range from 110°C up to 120°C during irradiation is favorable to crosslinking. At temperature higher than 125°C the degradation is predominant in comparison to the crosslinking.

Irradiation at elevated temperatures

An increase of the temperature induces different processes in the polymer bulk:¹⁸ faster decrease of the concentration of radicals induced by irradiation, decrease of addition reaction, increase of the frequency of β -scission reaction, increase of the chain diffusion to the amorphous phase, and partial melting of pellets. During this process the molecular chain architecture will be modified, depending on the temperature of irradiation.

Additionally, the melting and crystallization behavior of PP should be considered. The melting of certain parts of the polymer crystals starts with increasing temperature. Therefore, the crystallinity of the modified samples decrease. This leads to the conclusion that the amount of the amorphous phase rises and therefore more chains are available for branching reactions.¹⁸

In comparison to PP the temperature dependence of irradiation-induced reactions of polyethylene is described by Wu et al.,¹⁹ Qu et al.,²⁰ and Dijkstra et al.²¹ The irradiation of polyethylene at room temperature already can lead to the formation of insoluble parts. With increasing irradiation temperature up to the molten state, more crosslinking takes place. It is observed that an amount of gel up to 90% for low density polyethylene is possible.¹⁹

Influence of long chain branching on the SEC separation process

Molecular data of polyolefins can be extracted from measurements of the high temperature size exclusion chromatography (HT-SEC). It is well known that polymer molecules in SEC are separated by their hydrodynamic volume. The size of a molecule depends on its molar mass and on its density in the dissolved state. Long chain branched molecules have more dense structures than do linear molecules at the same molar mass. The density depends on the number of the branches. 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 the SEC with multiangle laser light scattering (MALLS) detector the molar mass of every slice of the chromatogram can be determined directly. Additionally, light scattering data give information about the radius of gyration of the molecules and their branching structure, respectively. The calculation of the parameter g known as Zimm-Stockmayer's branching parameter²² and the number of branching points along the trifunctional randomly branched molecule m ^{9,22} is described by Krause et al.²³

Influence of long chain branching on the rheological properties of polymers

Correlations between rheological properties and the molecular structure can be used to investigate the long chain branching topology. From measurements on rather well-defined long chain branched polymers^{24–28} some results were obtained, which allow insight into relationships between rheology and the topography of long chain branching. These correlations have been explained theoretically, e.g., the exponential dependence of the zero shear viscosity η_0 for star polymers on the ratio of M_a/M_e , i.e., the molar mass of an arm M_a divided by the entanglement molar mass M_e , according to the following equation^{29,30}:

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

The value of M_e is a characteristic quantity of a polymer and α and ν are constants in the order of 1 and 0.5, respectively. Gabriel et al.²⁴ concluded from investigations on a number of different commercial polyethylenes that slightly long chain branched PE with a star-like molecular structure come to lie above the values of linear PE whereas a position beneath indicates a highly branched tree-like topology. This was explained by the exponential dependence of η_0 on the ratio of M_a/M_e .

In elongational flow the occurrence of an increase of the elongational viscosity, which is called strain hardening, is closely related to molecular parameters and particularly, to long chain branching.^{10,31,32} If determined from stressing experiments this means that at a constant Hencky strain rate the elongational viscosity rises above the linear viscoelastic start-up curve given by three times the time dependent shear viscosity. The strain hardening behavior of randomly branched polyolefins is found to be characteristic for different branching topologies.^{10,31} Therefore, the rheological methods can be used to get a further insight into the evolving molecular structures.

Light scattering in solution and rheological experiments in the molten state are different ways to inves-

tigate long chain branching. The branching character, e.g., a star-, comb-, or a tree-like, cannot be detected directly by SEC-MALLS. For the characterization of the chain branching topology rheological experiments in elongation and shear flow can provide a hint. The aim of this work is to combine the results of these two methods to investigate the branching structure of the samples more thoroughly.

MATERIALS AND METHODS

Materials

The iPP homopolymer used in this study was Novolen PPH2150 (Basell Polyolefins Company N.V., Hoofddorp, The Netherlands). According to 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/cm³.

Electron beam irradiation

The iPP granulate was irradiated with 1.5 MeV, using an electron beam accelerator (ELV-2, Budker Institute of Nuclear Physics, Novosibirsk, Russia) described in detail by Dorschner et al.³³ The irradiation was carried out in a special vessel.³⁴ The sample was placed onto a support in this vessel, which includes heating elements and temperature sensors for temperature control. The irradiation was carried out under nitrogen at atmospheric pressure. Before the vessel was filled with nitrogen it was evacuated to 10⁻² Pa to minimize the concentration of oxygen.

Prior to the irradiation, the samples were heated up to a definite temperature, which has been retained unchanged during irradiation. The sample was irradiated with total doses of 20 and 100 kGy. Total doses were accomplished on a step-by-step basis with a dose of 10 kGy per pass to minimize the temperature increase, which results from the irradiation. It is to be beard in mind that during the irradiation process a certain heating-up of the samples takes place. At a dose rate of 10 kGy an increase of the temperature of ~5 K has to be expected. For this reason the experimental temperature implies a slightly higher value. Afterwards, the irradiated PP was annealed for 60 min at 130 or 150°C, respectively, to realize a deactivation of the residual radicals. The annealing step was carried out in the vessel under nitrogen atmosphere, too.

Size exclusion chromatography

The molecular characterization of the PP samples was carried out by HT-SEC. The instrument used was a PL-GPC220 (Polymer Laboratories Ltd., Church Stretton, UK) at 150°C equipped with a refractive index detector and coupled with a MALLS detector (DAWN EOS, Wyatt Technology Corp., Santa Barbara). The

column set consisted of two columns PL Mixed-B-LS, 300 × 7.5 mm², 10-μm particle size (Polymer Laboratories Ltd., Church Stretton, UK). The flow rate was 1 mL/min. The eluent was 1,2,4-trichlorobenzene (Merck KGaA, Darmstadt, Germany) stabilized with diphenylamine (Merck KGaA, Darmstadt, Germany) against the thermo-oxidative degradation of the polymer. The calculations of the molecular parameters (e.g., M_w , M_n , molar mass distribution, radius of gyration) were carried out from the SEC data using commercial software ASTRA 4.73 and CORONA V1.40 for Windows (Wyatt Technology Corp., Santa Barbara).

Differential scanning calorimetry

The differential scanning calorimetry (DSC) measurements were performed on a Q1000 (TA-Instruments, New Castle, USA) coupled with an autosampler in the temperature range of -60 to 210°C at a scan rate of ±10 K min⁻¹. Samples of about 5 mg were investigated under nitrogen atmosphere in a run cycle of 1st heating-cooling-2nd heating. The calibration of temperature and transition heat was done with an In standard. The glass transition temperatures were calculated using the half step method, and the crystallinity using the value of 207 J/g for 100% crystalline PP.³⁵

Rheology

The rheological measurements in shear were performed at a temperature of 180°C under nitrogen atmosphere using a rotational rheometer with plate-plate geometry of 25 mm in diameter and a gap of about 1.5 mm. The zero shear viscosity η_0 was determined from creep measurements at low shear stresses of around 10 Pa, i.e., in the linear range of deformation, using a constant stress rheometer (Malvern Instruments Ltd., Malvern, UK). Creep tests are very suitable for the determination of η_0 as the steady state of deformation is reached faster than in oscillatory or stressing experiments.³²

The elongational flow experiments were performed by means of an oil bath extensional rheometer. This device was self-constructed at the Institute of Polymer Materials and has been described in detail by Müntedt et al.^{32,36} For measuring the elongational viscosity a cylindrical sample is stretched vertically in a silicone oil bath. Constant strain rate experiments at a constant temperature of 180°C were conducted with different Hencky strain rates ε_H between 0.01 and 1.0 s⁻¹. The tensile stress growth coefficient or elongational viscosity is obtained from the measured tensile stress divided by the applied constant strain rate:

$$\eta_E^+(t, \dot{\varepsilon}_0) = \sigma(t, \dot{\varepsilon}_0) / \dot{\varepsilon}_0 \quad (2)$$

TABLE I
Molecular and Rheological Data of the Polypropylenes Investigated

Irradiation dose [d, kGy]	Irradiation temperature [T, °C]	Weight average molar mass [M_w , kg/mol]	Polydispersity [M_w/M_n]	Molar mass of segments [M_s , ^a kg/mol]	Zero shear viscosity [η_0 (180°C), kPas]
0	initial	669	4.2	—	188
20	25	411	3.0	189	107
20	80	404	2.7	180	73
20	110	411	2.6	145	60
20	150	385	2.8	117	51
20	170	385	2.9	95	38
20	190	379	2.6	95	29
20	210	309	2.6	83	17
100	25	244	3.3	31	5.5
100	50	240	3.3	31	3.2
100	80	235	3.3	30	2.1
100	110	222	3.7	26	1.7
100	130	212	3.5	22	1.3
100	150	218	3.8	19	1
100	210	101	3.8		

^aIt is calculated by SEC-MALLS, using eq. (5).

The strain hardening factor X_E is defined as the deviation from Trouton's law. It is determined according to the following equation:

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

RESULTS AND DISCUSSION

Molecular characterization

It was found that for the irradiation at elevated temperatures a slight decrease of molar mass took place (see Table I). If the samples were irradiated with 20 kGy at 25–190°C then the molar masses were nearly unchanged. And the irradiation of PP with 100 kGy at 25–150°C led to a slight decrease of molar mass (see Fig. 1). Only in case of 210°C a very high molar mass degradation takes place, caused by thermal degradation (see Table I). The molecular degradation was a hint of increased rate of β -scission reactions. It was found that in experiments with annealing of linear iPP at 210°C without irradiation do not lead to a molar mass degradation. This is shown in the comparison to cumulative molar mass distribution of the initial iPP and an annealed iPP under nitrogen atmosphere in Figure 1. The perceptible deviation of results lie within the limits of the experimental error of SEC-MALLS. One can conclude that such behavior can only be a result of the increase of the temperature during irradiation.

Figure 2 shows the dependence of the mean square radius of gyration on the molar mass for differently treated samples. After irradiation at 20 and 100 kGy, all samples show lower radii of gyration than that of the initial sample caused by the branching process,

which has taken place. Moreover, the decrease of the radius of gyration was clearly dependent on the irradiation dose and on the irradiation temperature. The samples irradiated at 25–80°C have the same radius of gyration and branching density, respectively. At temperatures above 110°C the radii of gyration were decreasing with irradiation temperature and this indicated a more pronounced branching and higher degree of long chain branching. This means that the temperature influenced the formation of long chain branching. A possible explanation for these effects is the different diffusion possibility of the chain fragments and the increasing amorphous phase depending on the temperature. Higher temperatures enable the better diffusion of the chain fragments followed by

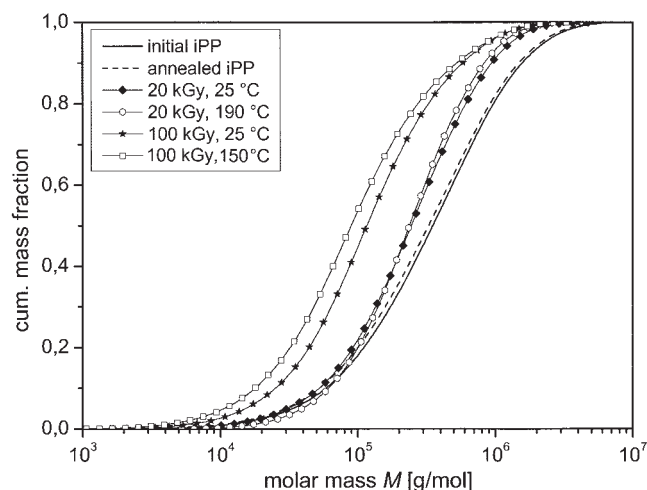


Figure 1 Cumulative molar mass distribution for initial iPP, annealed PP at 210°C, and for selected samples irradiated with 20 and 100 kGy.

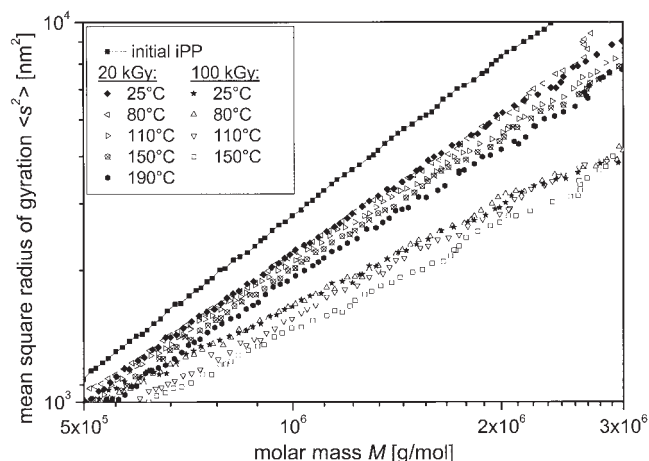


Figure 2 Mean square radius of gyration $\langle s^2 \rangle$ in dependence on molar mass M for the samples irradiated with 20 and 100 kGy.

formation of long chain branching with differently large chain fragments.

The influence of temperature on the branching structure with differently large chain fragments can be investigated with a calculation of the molar mass of arms or so-called length of long chain branching, respectively. Gabriel et al.²⁴ used the following equation to estimate the molar mass of long chain branching M_a for a low branched star-like structure:

$$M_a = \frac{M}{m + 2} \quad (4)$$

The value 2 was added to the number of long chain branches per molecules m to obtain correct values for the molar mass of long chain branches M_a . This equation describes a trifunctional three-arm star.²⁴ This calculation is only feasible for slightly branched poly-

mers with a star-like molecular structure. If a higher number of long chain branches per molecule m is found than the structure is similar to a comb- or tree-like architecture. For a highly branched polyolefin (e.g., LDPE) the molar mass of long chain branches M_a is estimated to be high if a star-like structure is assumed. In this case it is necessary to consider the chain segments between the different branching points along the molecules. The number of the inner segments between the branching points m can be described with the term $(m - 1)$. The term $(m + 2)$ describes the number of chains between branching points and chain ends per molecules. Therefore, the following equation is applied to calculate the molar mass of segments M_s :

$$M_s = \frac{M}{(m + 2) + (m - 1)} \quad (5)$$

Figure 3 shows a schematic illustration of a long chain branched molecule with three branching points. In this case one can observe two segments (s) between the different branching points and five segments (end) between branching point and chain end.

The resulting quantity M_s describes the average molar mass of segments per molecules. If the segments between branching points and chain ends are observed then this described the molar mass M_a or length of long chain branching. It cannot mirror the true structure. This estimation considers the assumed architecture of molecules and it is unessential to differ between comb- or tree-like (see Fig. 3).

The calculation of the molar mass of segments M_s [using eq. (5)] for irradiated samples supports the assumption of an influence of temperature on branching structure. Figure 4 shows the distribution of M_s over the whole region of the molar masses for selected

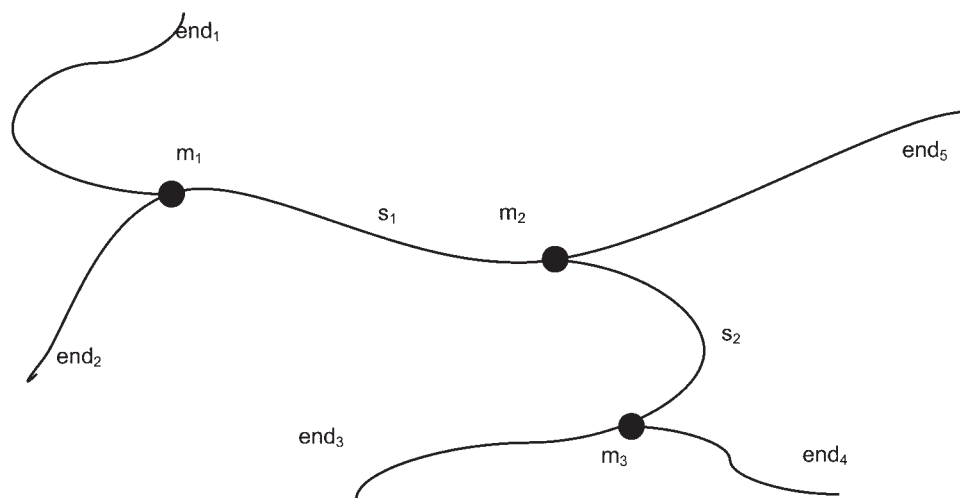


Figure 3 Schematic structure of long chain branched macromolecules.

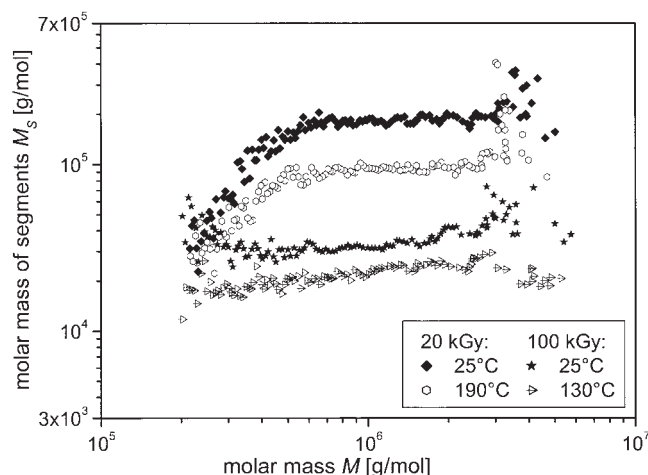


Figure 4 Molar mass of segments M_S in dependence on molar mass M for the selected samples irradiated with 20 and 100 kGy.

samples. M_S was found to be nearly constant in the range between 5×10^5 and 3×10^6 g/mol for all samples (see Fig. 4). This leads to the conclusion that the number of branching points along the molecule m correlates directly to the molar mass. The deviations of M_S from this constant value at lower and higher molar masses can be explained on the one hand with the limitations of the calculation method used in the applied commercial software. On the other hand at the beginning and at the end of the chromatographic separation process the concentrations of the polymer are presumably not sufficiently high for a correct interpretation of their light scattering properties and the calculation of their mean square radius of gyration, respectively. Hence, the constant central region of this curve was found to give us the appropriate value of the molar mass of segments M_S in this polymer. The values calculated for M_S are given in Table I and Figure 5 for the irradiated samples. The main decrease of the molar mass of segments M_S is observed with increasing the temperature about 110°C. For the samples irradiated with 100 kGy, M_S is about 31,000 g/mol in the temperature range of 25–80°C. By increasing the temperature up to 110°C M_S decreases to a value of 25,500 g/mol at the same molar mass of the polymer. At temperatures of 130 and 150°C, values of M_S about 22,000 and 19,000 g/mol, respectively, were determined. The same effect of temperature is observed for the sample irradiated at 20 kGy, too. In this case the molar mass of segments M_S decreases from 189,000 g/mol at 25–80°C up to 145,000 g/mol at 110°C and 95,000 g/mol at 170 or 190°C, respectively. If the value of M_S at 25°C is compared with the one in the molten state then M_S decreases to 50%.

These results are in good agreement with the assumption, that the temperature during the irradiation process plays an important role in the induction for

the rate of β -scission reactions in the polymer. At room temperature large chain fragments will predominantly arise, which react to form branched molecules with large arms. Therefore, this form is similar to low branched stars or combs. By increasing the temperature short chain fragments are expected to be formed predominantly. These fragments then can react with the main chain or already formed chain branches to create various branching structures. These structures can be described as higher branched ones. Consequently, the increasing of temperature gives a higher amount of shorter fragments followed by increasing the number of shorter branching arms.

Thermal analysis

In the present work, the irradiation temperature will be varied. Therefore, DSC measurements show the influence of heating the samples during irradiation on molecular properties. Furthermore, The influence of long chain branching on the melting and crystallization behavior and crystallinity of PP was investigated. For the samples irradiated with 20 kGy the characteristic temperatures are not changed significantly with irradiation temperature. Therefore, in this paper the melting and crystallization behavior is discussed only for the samples irradiated with a dose of 100 kGy.

The melting behavior of the initial PP is shown in Figure 6. The onset of the melting is at $\sim 100^\circ\text{C}$. It follows that the samples irradiated at about 100°C are partially molten. The molecular changes observed occur by irradiation about 110°C. This finding is associated with the increasing amorphous part and the improved diffusion of chains.

The glass transition temperature T_g of the samples irradiated at various temperatures was unchanged up to an irradiation temperature of 110°C. At higher ir-

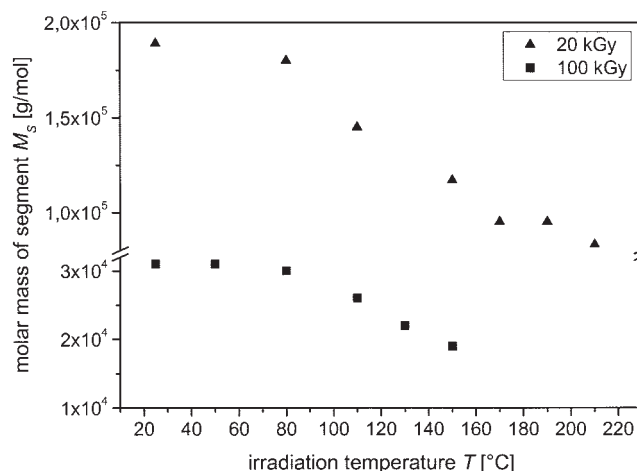


Figure 5 Molar mass of segments M_S in dependence on irradiation temperature T for the samples irradiated with 20 and 100 kGy.

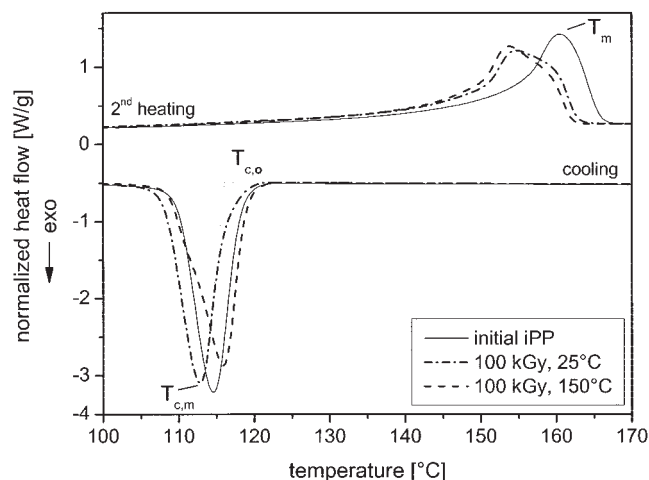


Figure 6 Normalized heat flow of 2nd heating and cooling for the initial iPP and the samples irradiated with 100 kGy at 25 and 150°C.

radiation temperatures T_g shifts to lower values. This is only a small tendency (see Table II). The crystallinity α was not influenced by the irradiation (see Table II). The melting peak temperatures T_m of all irradiated samples are lower than T_m of the virgin material (see Table II, Figs. 6 and 7) and were not influenced by the irradiation temperature (see Fig. 7). Therefore, the decrease of melting temperature after the irradiation should be caused by molar mass degradation and a reduced lamellae thickness due to the higher nucleation density.

At irradiation temperatures of 25 and 50°C the maximum crystallization temperature $T_{c,m}$ decreased after the irradiation. With increasing the irradiation temperature the crystallization temperature $T_{c,m}$ increased as well as the onset temperature $T_{c,o}$ (see Table II, Figs. 6 and 7).

Gahleitner et al.³⁷ described that long chain branching leads to a significant increase of the nucleation density, and consequently, to a higher crystallization temperature of the samples. Therefore, it is assumed that the reason for the observed earlier crystallization

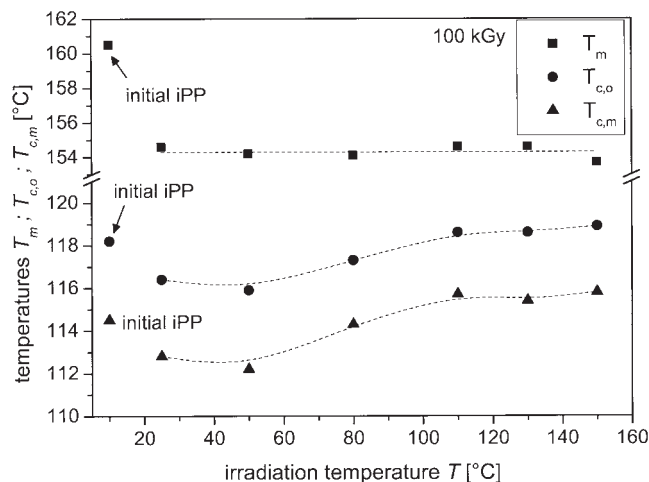


Figure 7 Melting peak temperature T_m of PP (2nd heating run), extrapolated onset and maximum crystallization temperature of PP $T_{c,o}$, $T_{c,m}$ in dependence on irradiation temperature T for the samples irradiated with 100 kGy.

is the existence of more long chain branching. It is improbable that the crystallization behavior is influenced by the molar mass of samples because the molar mass is nearly unchanged in its dependence on irradiation temperature. A higher crystallization temperature is particularly valuable in industrial applications for which an earlier solidification is desired because this leads to faster processing.

Rheological characterization in shear flow

Shear rheology is a very sensitive tool to detect even slight changes of the molecular structure and low amounts of long chain branching.^{23,24,38} This is particularly true for the zero shear viscosity if regarded as a function of weight average molar mass M_w .^{24,38} In Figure 8 the straight full line represents its power law dependence for a series of commercial linear iPPs.¹⁰ This relationship is also valid for the linear iPP, which was used for irradiation (star symbol). The zero shear viscosities η_0 of the samples irradiated with 20 and 100

TABLE II
DSC Data of Cooling and the 2nd Heating Run of PP Pellets Irradiated with 100 kGy

Irradiation temperature [T, °C]	Glass transition temperature [T _g , °C]	Melting enthalpy [ΔH _m , J/g]	Crystallinity [α, %]	Melting peak temperature [T _m , °C]	Maximum crystallisation temperature [T _{c,m} , °C]	Extrapolated onset crystallisation temperature [T _{c,o} , °C]
initial	-6.8	97.6	47	160.5	114.5	118.2
25	-7.7	98.8	48	154.6	112.8	116.4
50	-7.9	96.9	47	154.2	112.2	115.9
80	-7.7	99.0	48	154.1	114.3	117.3
110	-7.9	99.8	48	154.6	115.7	118.6
130	-8.0	99.4	48	154.6	115.4	118.6
150	-8.4	97.7	47	153.7	115.8	118.9

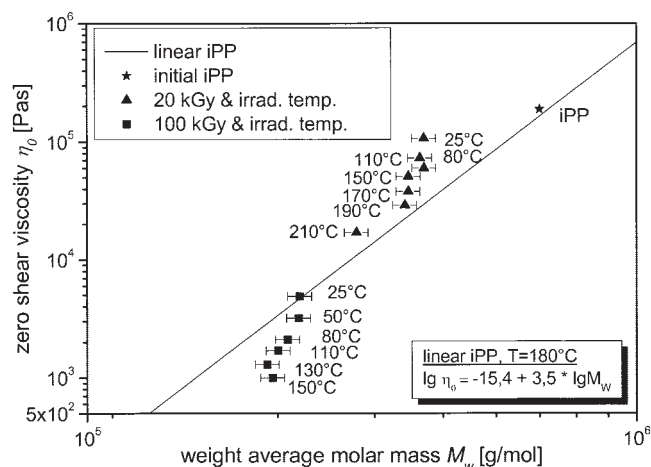


Figure 8 Zero shear viscosity η_0 in dependence on weight average molar mass M_w for the initial iPP and for the samples irradiated with 20 and 100 kGy.

kGy at different temperatures were found to deviate from this relationship (see Fig. 8). If compared with linear PPs of the same molar masses, very interesting results are obtained. The samples irradiated with 20 kGy are located above the line of linear iPP whereas those irradiated with 100 kGy are mainly beneath this line. For both series significantly decreasing zero shear viscosities η_0 with increasing irradiation temperature were observed (cf. Table I and Fig. 8). The significant reduction of the molar mass and zero shear viscosity of sample irradiated at 20 kGy and 210°C can be attributed to a pronounced thermal degradation.

A more quantitative comparison of the zero shear viscosities η_0 of branched and linear PP $\eta_{0(\text{br})}/\eta_{0(\text{lin})}$ at the same weight average molar masses M_w is given in Figure 9. From the exponential dependence of η_0 on the ratio of M_a/M_e it follows that the values greater than 1 for the samples irradiated at 20 kGy (25°C) point to molecular structures with relatively high molar masses of the long chain branches. For the samples irradiated with 100 kGy at 25°C the ratio $\eta_{0(\text{br})}/\eta_{0(\text{lin})}$ becomes nearly 1. It can be concluded that molecular structures are generated, which contain a higher number of branches with relatively small molar mass. From the statistical branching process it has to be assumed that these branches are randomly distributed along the backbone or side chains, respectively. Therefore, a tree-like topology is highly probable for samples irradiated at 100 kGy.

A significant reduction of the ratio $\eta_{0(\text{br})}/\eta_{0(\text{lin})}$ was observed for the samples irradiated at 20 and 100 kGy with increasing irradiation temperature. The decrease of $\eta_{0(\text{br})}/\eta_{0(\text{lin})}$ taken at the same M_w can formally be related to a reduction of the molar mass of arms M_a of the chain branching.^{25,39,40} But M_a cannot be measured or calculated directly from chromatographic measurements. However, for slightly branched molecules the

length of the outer segments with free ends corresponds to long chain branches attached to the backbone (cf. Fig. 3). For this reason, a relation of M_a to the segment molar mass M_S as calculated by eq. (5) can be assumed for the interpretation of the results. From Table I it can be seen that the segment molar mass M_S and hence the length of the chain branches becomes shorter with higher irradiation temperature. Using these model assumptions the decrease of $\eta_{0(\text{br})}/\eta_{0(\text{lin})}$ can be explained by the decrease of the molar mass of long chain branching.

The same conclusion on the change of the molar mass of the branches can be drawn using a model proposed recently by Inkson et al.⁴¹ for comb-shaped polyethylene. Hereby, the shift of the zero shear viscosity η_0 is described as a function of the number and length of the branching arms. It was found that both the decrease of the length of chain branching as well as the increase of the number of chain branching leads to a lower zero shear viscosity η_0 at the same weight average molar mass. Comparing the influence of both parameters on the zero shear viscosity the length of chain branching has the highest effect. Our observed results on the zero shear viscosity η_0 correlates well with the model predictions that η_0 decreases with increasing number of long chain branches and a decreasing molar mass of long chain branches.

Rheological characterization in elongational flow

The strain hardening behavior of branched polyolefins is found to be characteristic for different branching topographies.^{10,31} Therefore, this rheological method can be used to get a further insight into the molecular structures of the samples. The strain rate dependence of the elongational viscosity can be used to draw

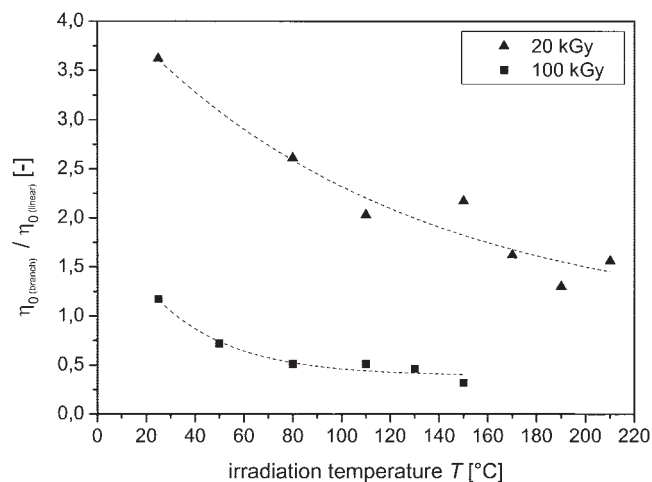


Figure 9 Ratio of the zero shear viscosities η_0 of branched and linear PP in dependence on the irradiation temperature T for the samples irradiated with 20 and 100 kGy.

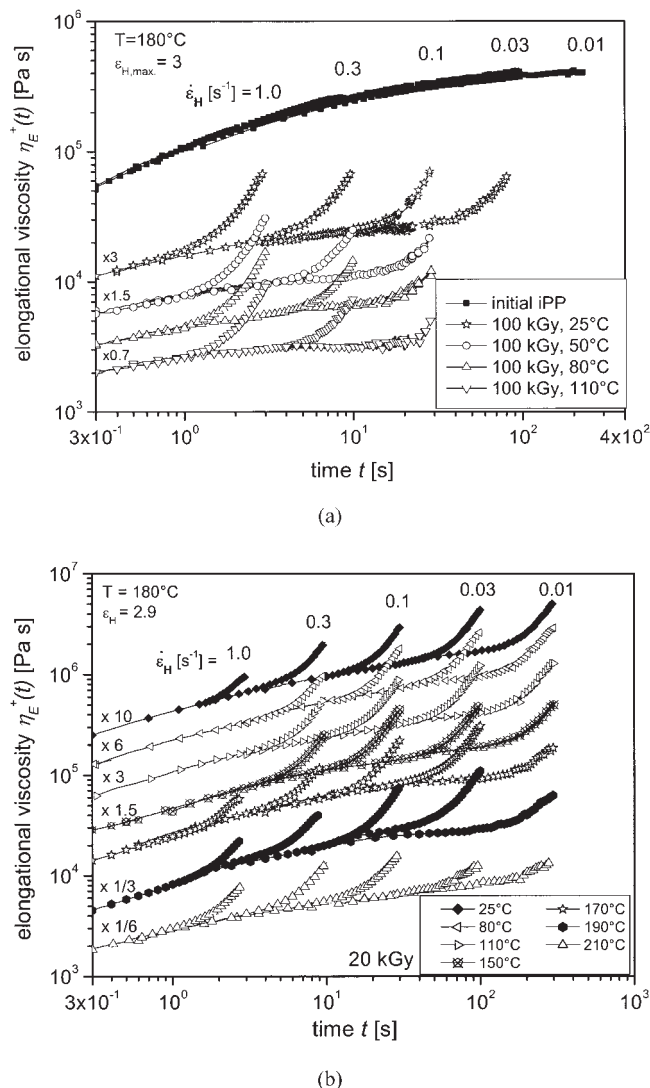


Figure 10 Elongational viscosity η_E in dependence on time t . (a) For the initial iPP and the samples irradiated with 100 kGy; (b) for the samples irradiated with 20 kGy.

further conclusions with respect to the topography of the various PP molecules, as the molar mass distributions are very similar. The cumulative molar mass distributions of different irradiated samples are shown in Figure 1. It was found that the molar mass distributions of irradiated samples were very similar (see Table I).

In elongational experiments, no strain hardening was found for the untreated linear iPP, which is consistent with results reported in literature for linear PPs of a similar molar mass distribution [Fig. 10(a)]. The samples irradiated with 100 kGy at 25–110°C show strain hardening, which increases with increasing strain rate [Fig. 10(a)]. This behavior is typically found for LDPE, having a high number of long chain branches and a tree-like molecular structure.^{31,42} Therefore, this dependence indicates a high degree of

branching with small arm molar masses M_a and it can be concluded that a highly branched topography is probable. The strain rate dependence did not change pointing to a similar molecular structure for the samples irradiated at various temperatures (see Fig. 11). This conclusion is supported by the only slight changes about 5000 g/mol calculated for the segment molar mass M_S (see Table I).

The samples irradiated with 20 kGy show a different strain hardening behavior, the strain rate dependence of which changes with rising irradiation temperatures [see Fig. 10(b)]. At low irradiation temperatures between 25 and 80°C the strain hardening factor X_E decreases with higher strain rates (Fig. 11). This dependence was found for metallocene catalyzed polyethylenes and points to a small degree of branching with high molar masses M_a of the branches.^{10,31} However, for temperatures of 110–190°C the strain hardening factor X_E runs through a maximum, which increases in height. A similar behavior was found for LDPE followed by increasing strain hardening with an increasing number of long chain branches determined as the number of CH_3 per 1000 C-atoms.⁴³ From the strain hardening factor X_E of the samples irradiated with 20 kGy it can be concluded that the number of branches increases while the length of branches decreases with irradiation temperature. The chromatographic measurements support this finding as the degree of long chain branching increases and the molar mass of segments M_S decreases from 189,000 g/mol at 25°C to 95,000 g/mol at 190°C.

Compared with the other samples irradiated with 20 kGy, for the highest applied temperature of 210°C the values at small elongation rates are very low between 1.5 and 2 and the strain hardening factor X_E increases with higher strain rates. This corresponds to

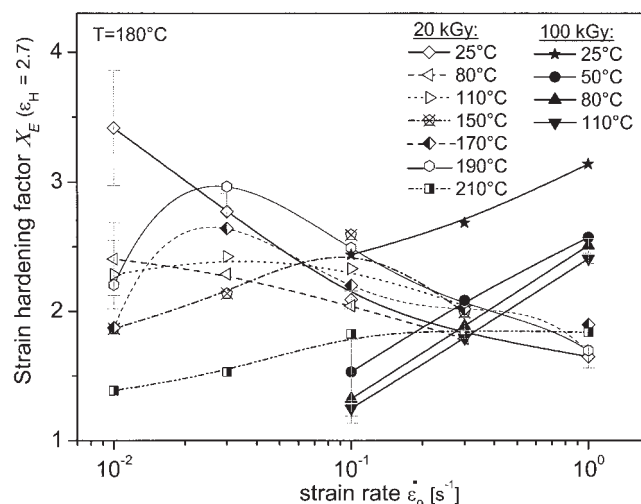


Figure 11 Strain hardening factor X_E in dependence on strain rate $d\epsilon_0/dt$ for the samples irradiated with 20 and 100 kGy.

the significantly lower molar mass and lower zero shear viscosity of the sample, which is originated from a pronounced degradation during irradiation. The behavior can be explained by low molar masses of the branches.

The error bars indicate the reproducibility of the experiments and from that it can be found that toward low strain rates the scattering increases. This can be attributed to the low tensile forces at large stretch ratios of the specimens since the force can be measured less accurate at smaller strain rates and lower viscosities.

CONCLUSIONS

It is known, that the modification of linear PP by means of electron beam irradiation is an efficient way to generate a long chain branched macromolecules. In this paper the influence of temperature during irradiation on molecular structure is described. Different effects by increasing the temperature of irradiation were found. This originates from reactions depending on temperature, such as β -scission or chain diffusion, and a partial melting of the pellets, which causes a change of crystallinity.

The observed results show a slight reduction of weight average molar mass M_w and an increase of the degree of long chain branching with increasing the irradiation temperature. At temperatures higher than 100°C the PP is partially molten followed by an increasing amorphous part. With it occurs that the chain branching reactions becomes more pronounced. If the samples are irradiated above 100°C, then a decrease of molar mass of segments M_S takes place. The molar mass of segments M_S is related to the length of long chain branching. That means that with increasing temperature the formed branched molecules have more and shorter long chain branching. The irradiation at 210°C leads to a significant molar mass degradation. Therefore, this irradiation temperature is too high for advantageous application.

Additionally, a shift of the crystallization maximum and of the onset temperatures toward higher temperatures is observed. This is attributed to the insertion of long chain branching. The irradiation of PP in the molten state regarding the molar mass, melting and crystallization behavior is described in more detail by Krause et al.⁴⁴

The investigation of rheological properties in shear and elongation clearly shows that molecular structure is changed by irradiation at different temperatures.

The results on the molar mass dependence of the zero shear viscosity indicate that the number of long chain branches is increasing and the molar mass of long chain branches is decreasing with irradiation temperature. From elongational rheology it can be concluded that the strain hardening characteristics of

the samples prepared by electron beam irradiation with 20 and 100 kGy are determined by the long chain branching topography. A change of molecular architecture from a slightly branched star-like type to a higher branched tree-like type is found for samples irradiated at 20 kGy. For the samples irradiated with 100 kGy it can be assumed that the type of topography did not change with increasing irradiation temperature since the strain rate behavior is very similar. The results from uniaxial elongation experiments support the conclusions from shear flow experiments that the irradiation at elevated temperatures results in a higher number of long chain branching with smaller values of M_a and are consistent with results from SEC.

The irradiation of PP at different temperatures is one way to generate long chain branched samples with different branching structure. Another way is using different irradiation doses in the range of 10–150 kGy at room temperature, resulting in a significant decrease of the ratio $\eta_{0(\text{br})}/\eta_{0(\text{lin})}$ and a changing strain rate dependence of the strain hardening. From that, it is concluded that the branching topology is changed from star-like to tree-like. Comparing the results from shear and elongational rheology it can be concluded that both the increase of irradiation dose at room temperature or the increase of temperature during irradiation at the same dose leads to an increasing degree of long chain branching. Therefore, it is possible to influence the branching structure not only by different irradiation doses but also by irradiation temperature. In both cases the branching topology can be varied. The combination of both irradiation parameters can be used to tailor the desired properties of a PP with respect to molar mass, long chain branching, and rheological behavior.

The authors thank the German Research Foundation (DFG) for financial support, M. Stephan for exchange regarding ideas to irradiation in molten state and U. Geißler and P. Treppe for the technical support.

References

1. Phillips, E. M.; McHugh, K. E.; Ogale, K.; Bradley, M. B. *Kunststoffe* 1992, 82, 671.
2. Park, C. B.; Cheung, L. K. *Polym Eng Sci* 1997, 37, 1.
3. Krause, B.; Häußler, L.; Voigt, D. *J Appl Polym Sci*, to appear.
4. Valenza, A.; Piccarolo, S.; Spadaro, G. *Polymer* 1999, 40, 835.
5. Sarcinelli, L.; Valenza, A.; Spadaro, G. *Polymer* 1997, 38, 2307.
6. Tobita, H.; Kawai, H. *e-Polymers* 2002, 48.
7. Rätzsch, M.; Bucka, H.; Hesse, A.; Reichelt, N.; Borsig, E. *Macromol Symp* 1998, 129, 53.
8. Lazar, M.; Hrkova, L.; Borsig, E.; Marcincin, A.; Reichelt, N.; Rätzsch, M. *J Appl Polym Sci* 2000, 78, 886.
9. Sugimoto, M.; Tanaka, T.; Masubuchi, Y.; Takimoto, J.; Koyama, K. *J Appl Polym Sci* 1999, 73, 1493.
10. Auhl, D.; Stange, J.; Münstedt, H.; Krause, B.; Voigt, D.; Lederer, A.; Lappan, U.; Lunkwitz, K. *Macromolecules* 2004, 37, 9465.
11. Scheve, B. J.; Mayfield, J. W.; DeNicola, A. J., Jr. (to Himont Inc.). U.S. Pat. 4,916,198 (1990).

12. DeNicola, A. J., Jr. (to Himont Inc.). Eur. Pat. 0,351,866 (1989).
13. DeNicola, A. J., Jr. (to Himont Inc.). Eur. Pat. 0,384,431 (1990).
14. DeNicola, A. J., Jr. (to Himont Inc.). U.S. Pat. 5,047,485 (1991).
15. Yoshii, F.; Makuuchi, K.; Kikukawa, S.; Tanaka, T.; Saitoh, J.; Koyama, K. *J Appl Polym Sci* 1996, 60, 617.
16. Rätzsch, M.; Hesse, A.; Bucka, H.; Reichelt, N.; Panzer, U.; Mehnert, R. (to Danubia Petrochem Polymere). Eur. Pat. 0,792,905 (1997).
17. Lawton, E. J. (to General Electric Company). Ger. Pat. 1,247,638 (1967).
18. Rätzsch, M.; Arnold, M.; Borsig, E.; Bucka, H.; Reichelt, N. *Progr Polym Sci* 2002, 27, 1195.
19. Wu, G.; Katsumura, Y.; Kudoh, H.; Morita, Y.; Seguchi, T. *J. Polym Sci Part A: Polym Chem* 1999, 37, 1541.
20. Qu, B. J.; Ranby, B. *Polym Eng Sci* 1995, 35, 1161.
21. Dijkstra, D. J.; Hoogsteen, W.; Pennings, A. *J Polymer* 1989, 30, 866.
22. Zimm, B. H.; Stockmayer, W. H. *J Chem Phys* 1949, 17, 1301.
23. Krause, B.; Voigt, D.; Lederer, A.; Auhl, D.; Münstedt, H. *J Chrom A* 2004, 1056, 217.
24. Gabriel, C.; Münstedt, H. *Rheol Acta* 2002, 41, 232.
25. Graessley, W. W.; Roovers, J. *Macromolecules* 1979, 12, 959.
26. Fetters, L. J.; Kiss, A. D.; Pearson, D. S.; Quack, G. F.; Vitus, F. *J. Macromolecules* 1993, 26, 647.
27. Wood-Adams, P.; Dealy, J. M.; deGroot, A. W.; Redwine, O. D. *Macromolecules* 2000, 33, 7489.
28. 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.
29. Pearson, D. S.; Helfand, E. *Macromolecules* 1984, 17, 888.
30. Ball, R. C.; McLeish, T. C. B. *Macromolecules* 1989, 22, 1911.
31. Gabriel, C.; Münstedt, H. *J Rheol* 2003, 47, 619.
32. Münstedt, H.; Kurzbeck, S.; Egersdörfer, L. *Rheol Acta* 1998, 37, 21.
33. Dorschner, H.; Jenschke, W.; Lunkwitz, K. *Nucl Instr Methods Phys Res B* 2000, 161–163, 1154.
34. Körber, H.; Lappan, U.; Geißler, U.; Lunkwitz, K.; Hanke, R. (to Institute of Polymer Research Dresden). Ger. Pat. 19,930,742 (2001).
35. Gaur, U.; Wunderlich, B. *J Phys Chem Ref Data* 1981, 10, 1051.
36. Münstedt, H. *J Rheol* 1979, 23, 421.
37. Gahleitner, M. *Prog Polym Sci* 2001, 26, 895.
38. Janzen, J.; Colby, R. H. *J Mol Struct* 1999, 485–486, 569.
39. Lagendijk, R.; Hogt, A. H.; Buijtenhuijs, A.; Gotsis, A. D. *Polymer* 2001, 42, 10035.
40. Münstedt, H. *J Rheol* 1980, 24, 847.
41. Inkson, N. J.; Read, D. J.; Kelmanson, M. A.; McLeish, T. C. B. In *Proceedings of 14th International Congress on Rheology*, 22–27 August 2004, Seoul, Korea.
42. Malmberg, A.; Gabriel, C.; Steffl, T.; Münstedt, H.; Löfgren, B. *Macromolecules* 2002, 35, 1038.
43. Münstedt, H.; Laun, H. M. *Rheol Acta* 1981, 20, 211.
44. Krause, B.; Stephan, M.; Volkland, S.; Voigt, D.; Häußler, L.; Dorschner, H. *J Appl Polym Sci* 2006, 99, 260.