



# Influence of various pretreatments on molecular and rheological properties of a linear and a long-chain branched polypropylene

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## Abstract

The influence of a mechanical or a thermal pretreatment of a linear (L-PP) and a long-chain branched polypropylene (LCB-PP) in the molten state was studied. The molar mass distributions and the branching structure were determined by high-temperature gel permeation chromatography HT-GPC coupled with laser-light scattering. The samples were extruded through long or short capillaries of various geometries corresponding to a predominant shear or elongational deformation. As a rheological probe, the extrudate swell at low stresses was measured for the differently pretreated samples. For the L-PP, neither molecular nor rheological changes were observed. However, the extrudate swell of the LCB-PP was found to decrease with increasing volume throughput. It was more strongly affected by shear in the capillary than by molecule stretching in the entry region. The smaller extrudate swell was accompanied by a decrease of the high molar mass tail of the LCB-PP, which could be the reason for the decay of swell, in principle. However, a comparable degradation of the high molar mass tail was obtained by a pure thermal treatment that was shown to leave the extrudate swell unchanged. This result and the unaffected branching structures found by high-temperature gel permeation chromatography (HT-GPC) support the hypothesis of a change of the branching topography by the mechanical pretreatment.

**Keywords** Linear polypropylene · Long-chain branched polypropylene · Mechanical pretreatment · Thermal pretreatment · Molecular analysis · Extrudate swell · Branching topography

## Introduction and motivation

Processability in the molten state has contributed a great deal to the technical and economical success of polymeric materials in the last decades. Injection molding and extrusion as the dominating processing operations are the base of mass production of many items from polymeric materials found nearly everywhere.

Already at the beginning of industrial manufacturing, it became obvious that thermal conditions and mechanical deformation occurring in the processing equipment may change the molecular structure of the polymeric materials and lead to a deterioration of end use properties (e.g. La Mantia et al. (2017)). These degradation processes are irreversible, and, thus, a lot of effort has been applied over the

years to optimize the processing parameters with respect to minimum degradation and to stabilize the materials by additives.

Considering these experiences and developments, two observations made in 1969 were surprising. For long-chain branched polyethylenes (Hanson (1969)) and for long-chain branched polyacetals (Prichard and Wissbrunn (1969)), it was found that the melt flow rate could be increased and the extrudate swell decreased by mechanical pretreatments in extrusion devices. Melt flow indices increasing with mechanical pretreatment are typical of molecular degradation due to chain scission, but the authors showed that the pretreatment effects on melt flow rate could be totally reversed by dissolution and subsequent precipitation of the polymer. Extensive studies of the mechanical pretreatment effect regarding the extrudate swell of a long-chain branched polyethylene and its reversibility were published by Rokudai (1979). For the linear counterparts of these materials, however, an influence of comparable mechanical pretreatments on rheological properties was not observed. These results were confirmed by

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several other authors over the years. A summary of early studies has been published by Rudin and Schreiber (1983).

But measurements of the molar mass distributions and the branching structures of pretreated polymers are very scarce in the literature, although they are essential for a deeper insight into the molecular mechanisms taking place. Such it is well known that molar mass distributions are changed by the strong extrusion conditions often applied to samples, and it is a matter of fact that this molecular degradation is not reversible.

The pretreatment effect is of interest from two points of view. Regarding applications, it improves processing and properties of manufactured items. For example, in case of LDPE, smaller thicknesses and improved optical properties of blown films could be achieved for the pretreated material in comparison to the initial resin (Hanson (1969)), Rokudai et al. (1979)). The other point of interest is a deeper understanding of the effect. As discussed by Münstedt (2021), some proposals are found in the literature, but a convincing explanation covering all known aspects has remained a challenge up to now.

In particular, the answers to two questions could support the search for a convincing model. The one is whether the pretreatment effect and its reversibility are restricted to long-chain branched polymers and the other whether shear or extension initiate the modification.

From a review of the literature and own studies on a linear and a long-chain branched polypropylene, it was concluded that the existence of long-chain branches is the most probable condition for the pretreatment effect (Münstedt (2021)). But from some few measurements on linear polyethylenes reported in the literature (Fu et al. (2019)), it may be concluded that it is also existent in linear species. However, in most cases, detailed molecular characterizations are missing. Ibar (2019) has compiled his extensive studies on linear polymers like polystyrene, poly(methyl methacrylate), polycarbonate, and linear low density polyethylene and has stated pretreatment effects using a special device that allows the superposition of strong shear, oscillatory, and elongational deformations. Furthermore, the shearing of samples in the nonlinear regime of plate-plate rheometry was used for pretreatments, and this device was applied subsequently for rheological characterizations in the linear viscoelastic regime. Molar mass distributions were shortly addressed, and it was mentioned that corrections of molecular changes were applied in cases of molecular degradations observed. However, the used procedures are often not described specifically enough to validate their results. Thus, the studies of pretreatment effects on linear polymers need further verifications and should be extended by comprehensive molecular characterizations to broaden the base for deeper insights.

Extensive studies on the effect of a mechanical pretreatment by extrusion on long-chain branched (LCB-PP) and linear (L-PP) polypropylenes and blends from them were

published by Gloger et al. (2022). The extrusion was performed under relatively mild conditions at an average shear rate of about  $100 \text{ s}^{-1}$ . Nevertheless, a degradation of the high molar mass component of the LCB-PP was found by gel permeation chromatography (GPC). As a rheological probe, dynamic-mechanical measurements and, in particular, those of  $G'$  were applied. A decrease of  $G'$  by extrusion was observed for the LCB-PP but not for the L-PP. This pretreatment effect was found to be only partly reversible by dissolving and subsequent precipitation of the extruded material. An influence of the degree of mechanical pretreatment on molecular and rheological properties was not reported.

Thus, the following studies address two essential open questions related to the mechanical pretreatment effect: role of molecular changes (molar mass distribution, branching architecture) and influence of deformation mode (shear or elongation). To discuss the first topic, a linear and a long-chain branched polypropylene were studied, and their molecular structures before and after various treatments were characterized. For the mechanical pretreatment, capillary rheometry was used to expose larger amounts of material to deformations stronger than those attainable in elongational and rotational rheometers.

Prevailing extension was achieved by the use of orifices and dominating shear with long capillaries. Additionally, a thermal pretreatment of the polypropylenes was applied to study the molecular changes without mechanical deformation and to compare the effects on extrudate swell with those of the extruded samples.

## Experimental

### Materials

Two commercial polypropylenes with different molecular architectures were chosen. The linear sample (L-PP) had a weight average molar mass  $M_w = 444 \text{ kg/mol}$  and a polydispersity index  $M_w/M_n = 4.5$ . The corresponding data for the long-chain branched polypropylene (LCB-PP) were  $M_w = 1090 \text{ kg/mol}$  and  $M_w/M_n = 18$ .

### Molecular characterization

Molecular characterization of the mechanically pretreated samples was performed using high temperature gel permeation chromatography HT-GPC (Agilent PL 220) in 1,2,4- trichlorobenzene (TCB) at  $140^\circ\text{C}$  and a flow rate of  $0.5 \text{ ml/min}$  together with low shear columns (UT 807, three UT 806M; Shodex) for separation. The HT-GPC was coupled with multi- angle laser light scattering (MALLS; Dawn EOS, Wyatt Technology) to measure absolute molar masses and coil dimensions. The refractive index detector of the

HT-GPC served as the concentration detector (refractive index increment  $dn/dc = 0.100 \text{ cm}^3/\text{g}$ ). Solutions were prepared at a concentration of 2 g/l. All results shown are mean values from at least three tests.

For the GPC measurements shown in the paragraph on thermal pretreatment, the equipment used for the data on the mechanically pretreated samples was not available anymore. The Dawn EOS was replaced by a DAWN NEOS, and the Shodex columns were changed to 4 POLEFIN columns (Agilent PSS). The flow rate was set to 1.0 ml/min.

Consequently, the separation characteristics are not the same, anymore, and the molar mass distributions and conformation plots obtained from the two systems can only qualitatively be compared.

## Rheological characterizations

Due to the decrease of molar mass by the pretreatments and its strong effect on viscous properties, elastic quantities have advantages for rheological characterizations that, as well known, are not influenced by molar mass above a certain value (e.g. Münstedt and Schwarzl (2014)).

Amongst them, the extrudate swell is very suitable for the characterization of the mechanically pretreated samples due to the convenient practicability and sensitivity of its determination. The state of the art is discussed in a review article by Tang et al. (2020), for example, and the importance of annealing the extruded strand for reliable data on extrudate swell is pointed out.

The measurements on the polypropylenes were carried out with an adapted melt flow indexer. The length to diameter ratio  $L/D = 4$  of the capillary and the piston load were kept constant resulting in an apparent constant wall shear stress of around  $5 \cdot 10^4 \text{ Pa}$ . The preheating time was 4 min at the measuring temperature of 180 °C. The strands were extruded into a water/ethanol mixture of adapted density to reduce sagging. Subsequently, they were annealed in a silicone oil bath at 180 °C for 30 min to attain the equilibrium values of the extrudate swell  $S$ , which is determined according to

$$S = d/D - 1 \quad (1)$$

where  $d$  is the diameter of the annealed strand and  $D$  that of the capillary.

## Modes of mechanical pretreatment

In the literature, various rheological methods were used to apply mechanical pretreatments to polymers in the molten state. From a fundamental point of view, it would be interesting to study mechanical pretreatments by pure shear or

elongation. The suitability of corresponding techniques is shortly discussed in the following.

## Oscillatory shear

In principle, pure shear could be applied in a plate-plate rheometer. Such experiments were performed by Ibar (2019) in oscillatory shear at high amplitudes. However, in case of PP, it was shown by Münstedt (2021) and for PS by Mattes et al. (2008) that the modulus decay taken as an indication of mechanical pretreatment effects was accompanied by fractures at the rim of the sample. Thus, this method was not used in this study.

## Uniaxial elongation

Uniaxial elongation represents another well-defined deformation mode. Experiments of this kind can be performed using the MTR rheometer as demonstrated, for example, on an LDPE (Münstedt (1981)). The effects were small, however, due to the restricted total elongations and elongational rates applicable in this laboratory device. Additionally, stretching experiments have the disadvantage of elaborate sample preparation and provide a relatively small amount of material for subsequent comprehensive characterizations.

## Capillary rheometry

Due to the limitations in applicability of the two methods described above, the potential of capillary rheometry was considered with respect to mechanical pretreatments of polymer melts. As it is obvious, the entrance flow from the barrel of a rheometer into a capillary comprises an appreciable amount of elongational deformation, whereby the flow within the capillary is dominated by shear. Choosing suitable capillary geometries, the amount of the two deformations and their ratios can qualitatively be adapted. In long capillaries, shear is prevalent, and for orifices, the extensional flow in the entrance region is dominant.

Furthermore, the rate of the two deformation modes can be changed in a wide range by the throughput chosen. Some corresponding relations supporting the assessment of the influences of flow in the entrance region and the capillary itself on the mechanical deformation of a melt are given in the Appendix.

Two capillaries with length to diameter ratios  $L/D = 40/1$  and  $30/0.5$  and an orifice with  $L/D = 2.5/0.5$  were used for the pretreatments. Most of the experiments were performed with a barrel of 9.5 mm, some others with a barrel of 12 mm in diameter that for a fixed capillary enables comparably larger stretching ratios in the entrance region according to Eq. (A8). The entry angle was 180°. Apparent shear rates

$\dot{\gamma}_a$  from  $720 \text{ s}^{-1}$  to  $14,400 \text{ s}^{-1}$  according to Eq. (A1) were applied.

The different pretreatments are indicated by the sample labeling. For example, LCB-PP 40/1-14,400 designates the long-chain branched PP that was extruded through a capillary with  $L/D = 40/1$  at an apparent shear rate of  $\dot{\gamma}_a = 14,400 \text{ s}^{-1}$ .

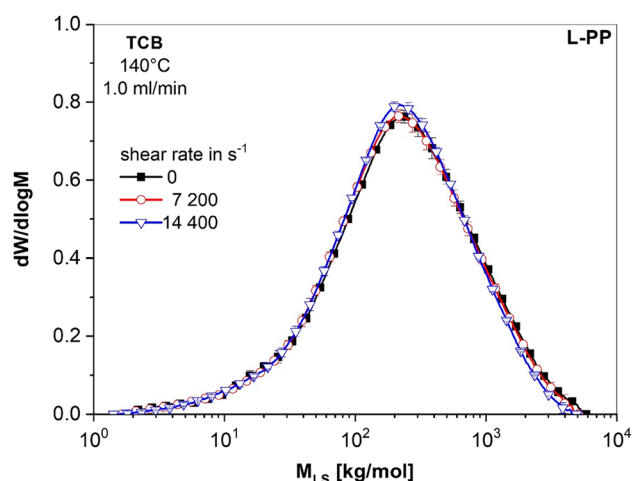
## Results

### Mechanical pretreatment

#### Influence of the mechanical pretreatment on molecular structure

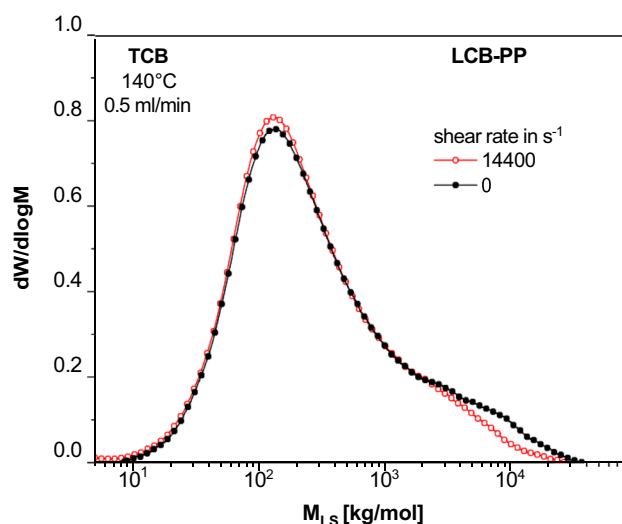
The large stress during mechanical pretreatment particularly at high shear rates may lead to a degradation of molecules that determine rheological properties. In order to get an insight into molecular changes due to mechanical pretreatments, molar mass distributions of the materials extruded at various shear rates in the capillary rheometer were measured by high-temperature gel permeation chromatography (HT-GPC).

The molar mass distribution of the neat L-PP and the samples extruded through the capillary of the rheometer at the two highest shear rates are shown in Fig. 1. There is a faint tendency of the long molecules becoming shorter with increasing rate, but the shape of curves representing the molar mass distribution, which decisively determines elastic properties, can be considered to remain unchanged within the accuracy of the measurements.



**Fig. 1** Molar mass distributions of the neat L-PP and samples after shearing at  $7,200$  and  $14,400 \text{ s}^{-1}$  through a capillary with  $L/D=40/1$  at  $T=180^\circ\text{C}$

The molar mass distribution of the LCP-PP, which is distinctly broader than that of the L-PP, is significantly affected, however, by extrusion through a capillary as shown in Fig. 2. At the shear rate of  $14,400 \text{ s}^{-1}$  applied, a decrease of the high molar mass tail becomes distinctly visible. The characteristic molecular data are shown in Table 1.  $M_w$  decreases with the mechanical pretreatment, but surprisingly  $M_w/M_n$  does not change within the accuracy of the measurement. This may be due to a slight broadening of the molar mass distribution at its lower end by the mechanical pretreatment that is not resolved by the equipment in use. Thus, in case of the broadly distributed long-chain branched LCB-PP, the polydispersity index is not a suitable quantity for getting insight into the pretreatment effect. Instead, the influence of the distinct change of the high molar mass tail on extrudate swell as the preferred rheological probe for studying the effect of mechanical pretreatment has to be discussed for the LCB-PP.



**Fig. 2** Molar mass distributions of LCB-PP as delivered and after shearing at  $180^\circ\text{C}$  and  $14,400 \text{ s}^{-1}$  through a capillary with  $L/D=40/1$

**Table 1** Weight average molar mass  $M_w$ , number average molar mass  $M_n$ , and polydispersity index  $M_w/M_n$  for the long-chain branched polypropylene LCB-PP as delivered and after extrusion through a capillary with the length to diameter ratio  $L/D=40/1$  at the apparent shear rate  $14,400 \text{ s}^{-1}$  and  $T=180^\circ\text{C}$ . The extruded sample is marked by “CR”

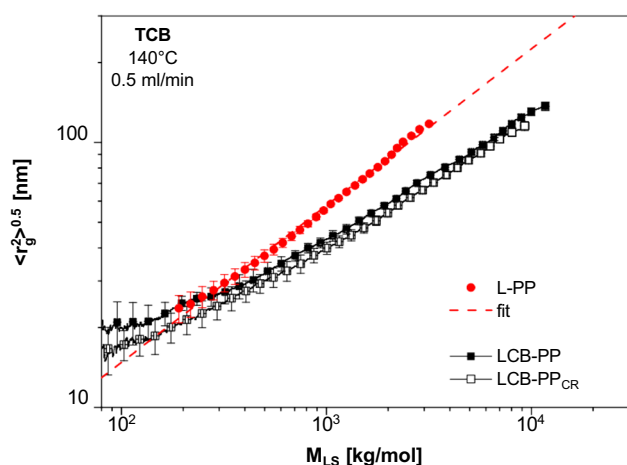
Material	$M_w$ [kg/mol]	$M_n$ [kg/mol]	$M_w/M_n$
LCB-PP	$1090 \pm 30$	$61 \pm 2$	$17.9 \pm 1.0$
LCB-PP <sub>CR</sub>	$804 \pm 20$	$44 \pm 5$	$18.3 \pm 1.8$

Another property that affects elastic quantities like extrudate swell is the branching structure of a polymer. For the branching analysis of the polypropylenes, gel permeation chromatography coupled with multi-angle laser-light scattering was applied as described in the previous section on experimental methods. The results are shown in Fig. 3. For the untreated and the extruded L-PP, the expected values of the radius of gyration as function of the molar mass come to lie on the same curve, the power-law exponent of which is in agreement with values reported in the literature. The curve for the LCB-PP is distinctly lower than that of the L-PP indicating long-chain branching due to coil contraction. At low molar masses, the resolution of the MALLS of 20 nm limits the measurements as shown by the increasing uncertainties in this regime. The measurements for the non-treated and the extruded LCB-PP do not exhibit significant differences over a wide range of molar masses.

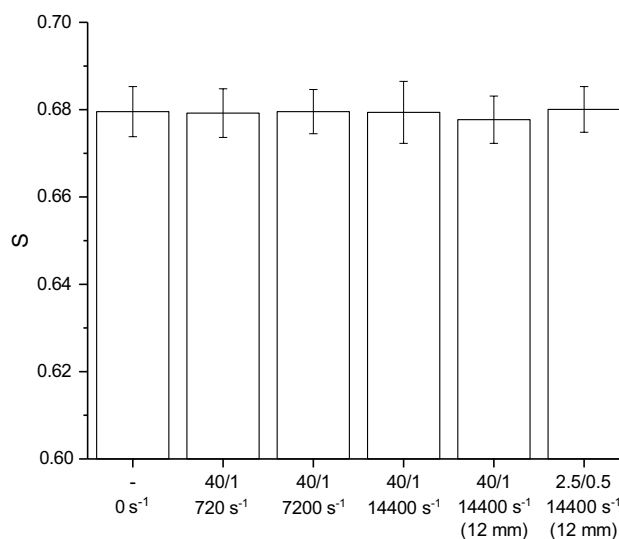
This result demonstrates that the branching structure determined in the highly diluted state was not changed by the extrusion through the capillary. It is in agreement with the findings on two similar polypropylenes mechanically pretreated in a twin-screw extruder (Münstedt (2021)).

### Effect of various extrusion parameters on extrudate swell

The L-PP was extruded through the capillary with  $L/D = 40/1$  and the orifice with  $L/D = 2.5/0.5$  at  $180^\circ\text{C}$  and the apparent shear rates shown in Fig. 4. Two barrels of 9.5 and 12 mm in diameter were used. The extrudate swells measured as described above and presented according to Eq. (1) were the same and equal to the value of the non-extruded



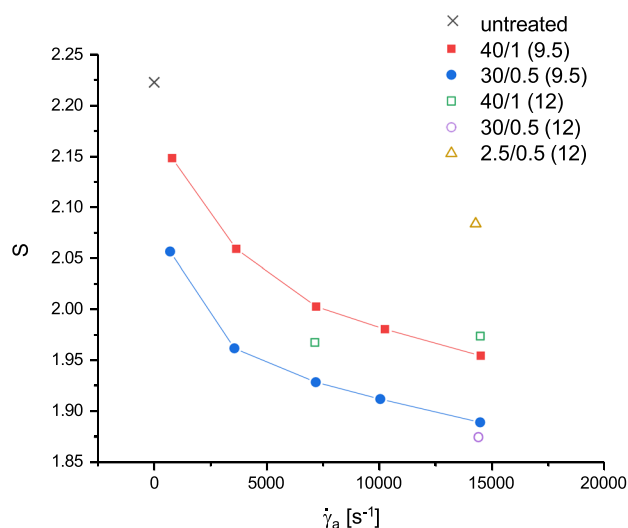
**Fig. 3** Expected value of the radius of gyration  $\langle r_g^2 \rangle^{0.5}$  as function of the molar mass  $M_{LS}$  measured by laser light scattering for the untreated L-PP and LCB-PP and the sample extruded at the highest shear rate of  $14,400\text{ s}^{-1}$  and  $L/D=40/1$  marked by the suffix “CR”



**Fig. 4** Extrudate swell  $S = d/D - 1$  of the L-PP pretreated by extrusion in the capillary rheometer at various conditions. The barrel diameter was predominantly 9.5 mm, but 12 mm where indicated. The conditions of measurement are given in the experimental section

sample. That means, the various mechanical pretreatments applied in the capillary rheometer did not have any influence on the extrudate swell of the L-PP.

Similar studies on the LCB-PP lead to totally different results as follows from Fig. 5, which exhibits the extrudate swell after pretreatments at several apparent shear rates  $\dot{\gamma}_a$  with various capillary geometries. The extrudate swell is not independent of the treatment any more like for the L-PP, but distinctly decreases with the previously applied



**Fig. 5** Extrudate swell  $S = d/D - 1$  of the LCB-PP in dependence on the apparent shear rates  $\dot{\gamma}_a$  in capillaries of various  $L/D$  and entry geometries (barrel diameters in brackets). The lines are drawn to guide the eye



$\dot{\gamma}_a$ . Already at the smallest shear rate of  $720 \text{ s}^{-1}$ , a value lower than  $S = 2.23$  for the untreated sample is found. The decline becomes more pronounced by raising the shear rate and reaches around 15% at  $\dot{\gamma}_a = 14,400 \text{ s}^{-1}$  for the capillary with  $L/D = 30/0.5$ .

The decrease of the extrudate swell for the capillary with the larger  $L/D = 30/0.5$  is significantly stronger than that of the capillary with  $L/D = 40/1$ . Increasing the extensional deformation in the entrance region by enlarging the barrel diameter from 9.5 to 12 mm has an only marginal effect on the extrudate swell for both capillaries and does not exhibit a clear tendency (see open symbols in Fig. 5). As Fig. 5 demonstrates, the extrusion through the orifice with  $L/D = 2.5/0.5$  at  $14,400 \text{ s}^{-1}$  leads to a comparatively smaller reduction of the extrudate swell than for the longer capillaries. Thus, the conclusion may be drawn that for the die geometries and the experimental conditions chosen, the pretreatment under shear within the capillary is more effective than the elongational deformation in the entrance region.

The role of shear for the mechanical pretreatment is supported by the fact that the extrusion through the capillary with the larger  $L/D = 30/0.5$  and, consequently, the higher shear effects a stronger reduction of extrudate swell than that within the capillary of  $L/D = 40$ .

For an interpretation of these results with respect to the effects of the mechanical pretreatments, it is necessary, however, to get an idea, how the extrudate swell used as the rheological probe is influenced by the molecular changes of LCB-PP connected with the capillary flow as shown in Fig. 2.

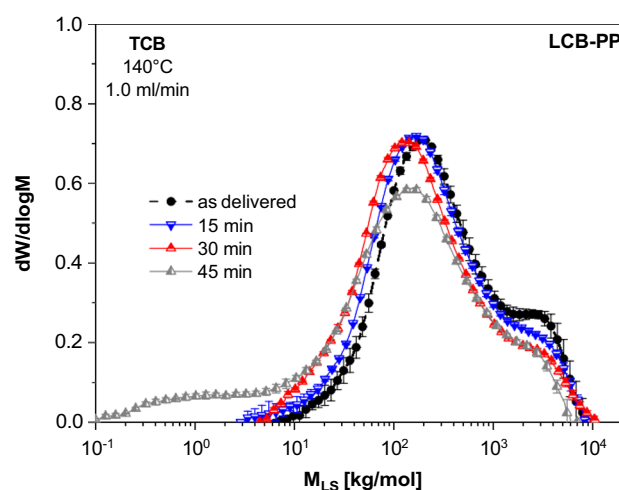
## Influence of thermal treatment

To address this question, samples were studied whose molar mass distributions were altered by thermal degradation excluding any appreciable deformation of the melt. For this purpose, the LCB-PP was exposed to a heat treatment at  $240^\circ\text{C}$  in the chamber of a laboratory mixer under nitrogen atmosphere for the residence times of 15, 30, and 45 min at 5 revolutions per min of the rotor. After cooling to room temperature, the kneaded material was chopped and filled to the melt flow indexer for the measurement of the extrudate swell as described in the previous section “Rheological characterization”.

Additionally, the molar mass distributions were determined by HT-GPC.

## Molecular characterization

Figure 6 shows the GPC curves of the samples as delivered and after thermal treatments of 15, 30, and 45 min at  $240^\circ\text{C}$ .



**Fig. 6** Molar mass distribution of the LCB-PP as delivered and after heat treatments of 15, 30, and 45 min at  $240^\circ\text{C}$  in a laboratory mixer

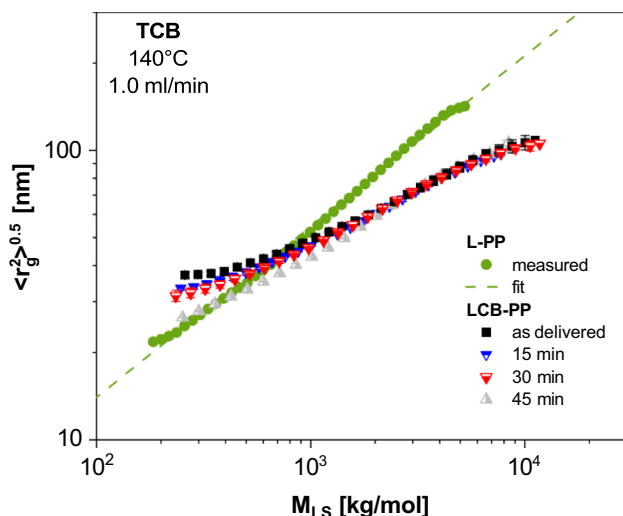
The distinctive high molar mass tail of the untreated LCB-PP is significantly decreased after 15 min already and further declines with longer treatment times. In parallel, the amount of low molar masses becomes more pronounced, especially at 45 min exposure time.

The characteristic molecular data are listed in Table 2.  $M_w$  significantly decreases with the duration of heat treatment as expected. The polydispersity index  $M_w/M_n$  is found to continuously increase and reflects the pronounced broadening of the molar mass distribution at low molar masses.

Figure 7 exhibits the expected value of the radius of gyration as a function of the molar mass similar to Fig. 3. As pointed out before, the column separation is different from that underlying Fig. 3. This feature becomes particularly evident from the low molar mass regime of the LCB-PP samples. It is known that for polymers containing high molar masses and/or high degrees of branching, non-ideal separation may occur (Netopilik and Podzimek (2020)). In this case, those molecules co-elute with molecules of low molar masses giving rise to an upswing of the radius of gyration at low molar masses. Nevertheless, from the experimental results in Fig. 7, it can be concluded that—in contrast to the

**Table 2** Weight average molar mass  $M_w$ , number average molar mass  $M_n$ , and polydispersity index  $M_w/M_n$  for the long-chain branched polypropylene LCB-PP as delivered and after thermal treatments at  $240^\circ\text{C}$  for 15, 30, and 45 min indicated by the corresponding suffix

Material	$M_w$ [kg/mol]	$M_n$ [kg/mol]	$M_w/M_n$
LCB-PP	$863 \pm 20$	$69 \pm 2$	$12.4 \pm 1.7$
LCB-PP <sub>15</sub>	$742 \pm 6$	$50 \pm 1$	$14.9 \pm 1.3$
LCB-PP <sub>30</sub>	$640 \pm 8$	$37 \pm 1$	$17.5 \pm 0.2$
LCB-PP <sub>45</sub>	$507 \pm 16$	$13 \pm 1$	$39.4 \pm 1.5$



**Fig. 7** Expected value of the radius of gyration  $\langle r_g^2 \rangle^{0.5}$  as a function of the molar mass  $M_{LS}$  measured by light scattering for the LCB-PP as delivered and heat treated at 240 °C for 15, 30, and 40 min, respectively. The broken line represents the relation for the linear PP from the literature

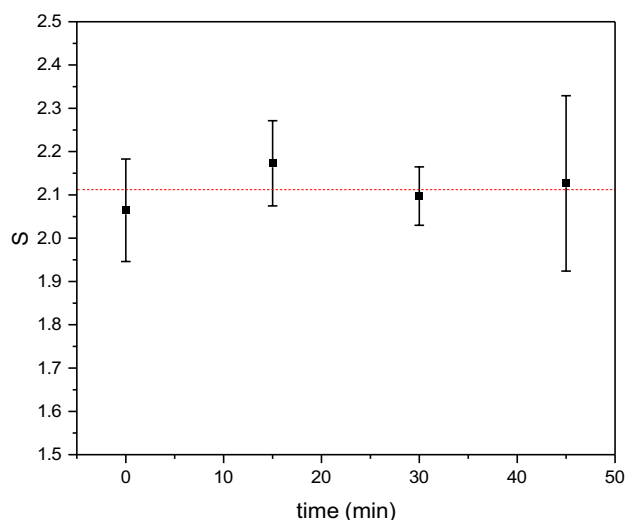
molar mass—the long-chain branch topography, reflected by the coil contraction at higher molar masses, was not affected by the thermal treatment.

### Extrudate swell

Of special interest with respect to the topic of this paper is the influence of the molecular changes observed on the extrudate swell used as the rheological probe. Thus, the LCB-PP previously exposed to the thermal treatment in the chamber of the laboratory mixer was filled to the melt flow indexer, and the extrudate swell was determined according to the experimental procedure described before.

The results of the thermal treatments on the extrudate swell are shown in Fig. 8.

This figure shows that within the accuracy of the measurements, the extrudate swell is independent of the thermal exposure and, thus, of the molecular changes shown in Fig. 6. From this result, it may be concluded that the extrudate swell of the broadly distributed LCB-PP is not dependent on the molar mass distribution and the high molar mass tail of the sample, in particular. At a first glance, this result seems to be in contrast to findings on other polymers like polystyrene, for example. For this material, it is shown that the extrudate swell increases if the molar mass distribution is broadened (Münstedt and Schwarzl (2014)). But there are two essential differences between PS and LCB-PP. PS does not contain long-chain branches, and its molar mass distributions are distinctly narrower.



**Fig. 8** Extrudate swell  $S = d/D - 1$  of LCB-PP after different durations of heat exposure at 240 °C in the chamber of the laboratory mixer. The measuring conditions of the extrudate swell are given in the “Rheological characterizations” section

The great influence of long-chain branches on elastic properties, which are reflected by the extrudate swell used as the rheological probe in this study, is supported by measurements of the time-dependent elastic compliance that can directly be determined from creep experiments in shear (Gabriel and Münstedt (1999)). The elastic compliance was measured in the linear range of deformation for a linear and a long-chain branched polyethylene with very similar molar mass distributions. Introducing long-chain branches enhances the recoverable compliance by about a factor 10. This result demonstrates the dominant role of long-chain branches for elastic properties of polymer melts and throws a light on the finding that the distinct reduction of the high molar mass tail of the LCB-PP by the applied thermal treatments shown in Fig. 6 is not reflected by the extrudate swell presented in Fig. 8.

These results are a strong argument for the conclusion that the decrease of swell with stronger mechanical pretreatment by extrusion through capillaries as shown in Fig. 5 is not due to the change of the molar mass distribution exemplarily given in Fig. 2. Rather, the postulate of a special pretreatment effect due to a deformation of the molecular network built up by the long-chain branches as discussed below is supported.

### Discussion

One of the obvious results is that the pretreatment by capillary flow, which significantly changed the elastic rheological property of extrudate swell in case of the

LCB-PP, did not show any influence on the L-PP. This behavior is in agreement with the studies on very similar materials using a twin-screw extruder for the pretreatment and various rheological properties like zero-shear viscosity, linear steady-state recoverable compliance, thermorheological complexity, and strain hardening as rheological indicators of changes (Münstedt (2021)). These quantities did not show an influence of the mechanical pretreatment on the L-PP but significant effects for the LCB-PP. Furthermore, the modification of the LCB-PP confirms the studies on other long-chain branched polymers from the literature that were mechanically pretreated in various ways and characterized by different rheological methods.

For the L-PP, an influence of the extrusion through the capillary on extrudate swell was not found. The obvious general postulate of a missing mechanical pretreatment effect for linear polymers derived from the findings on L-PP needs more experimental support, however, because some authors report modifications of linear species but others not as discussed by Münstedt (2021).

For a thorough discussion of the effect of mechanical pretreatment on the rheological behavior and on elastic properties in particular, the change of the molecular structure has to be considered and its influence on the used rheological probes critically assessed. This has only been done very qualitatively in few papers (e.g. Gloger et al. (2022)), and, thus, the experimental results going along with the molecular characterizations in parallel as described in this paper are thought to be an essential contribution to deeper insights into the mechanical pretreatment effect.

As Fig. 3 demonstrates, the branching structure characterized by the radius of gyration is the same before and after the mechanical pretreatment applied, and that also holds for the thermal treatment carried out as demonstrated in Fig. 7. However, this finding from the highly diluted state only shows that no irreversible change of the branching structure has occurred, but it does not say anything about the topography of branched molecules in the molten state generated by the mechanical pretreatment.

Strong deformations in the molten state—and these are the precondition for a measurable pretreatment effect—may degrade polymer molecules. For the LCB-PP extruded through capillaries, it is shown in Fig. 2 that the high molar mass tail becomes less pronounced after extrusion at the high shear rate and, thus, the average weight molar mass decreases. From the literature, it is well known that high molar mass components can lead to a very significant rise of the elasticity of a polymer melt, particularly when they are clearly separated from the molar mass of the matrix (e.g. Münstedt and Schwarzl (2014)). This means that a degradation of such a high molar mass component could lead to decreasing elastic properties. Thus, the extrudate swell of

LCB-PP becoming smaller with extrusion as shown in Fig. 5 could principally be due to molar mass degradation and not to a special pretreatment effect changing the interactions between molecules. The experiments of a purely thermal pretreatment of the PP-LCB demonstrated, however, that the high molar mass tail was significantly reduced and the molar mass distribution broadened, but the extrudate swell mainly determined by the long-chain branches remained the same going along with an unchanged branching structure according to HT-GPC. These findings demonstrate that the decrease of elastic properties may be related to mechanically induced changes of molecular interactions and not to degradation.

Another interesting result of this work on LCB-PP is, that shear in the capillary flow chosen leads to a distinctly more significant pretreatment effect than elongation in the entrance region. This seems to be in contrast to the findings on LDPE reported by Münstedt (1981). In that work, samples were sheared in a parallel-plate rheometer at a shear rate of  $\dot{\gamma} = 500 \text{ s}^{-1}$  up to a total shear of  $\gamma = 20$  or alternatively extended in a laboratory rheometer at an elongational rate of  $\dot{\epsilon} = 0.2 \text{ s}^{-1}$  up to stretching ratios of  $\lambda = 10$  or 25, respectively. The pretreated samples were rheologically characterized in creep tests at a constant tensile stress of  $\sigma = 10^4 \text{ Pa}$  up to the steady state. The elongational viscosity used as the rheological probe became lower with the previous extension, but remained unchanged within the accuracy of the measurement after the shear pretreatment applied. Molecular characterizations of the samples were not performed.

For a detailed discussion, it has to be considered that the mechanical pretreatments reported for LDPE and those on LCB-PP of this work differ significantly. According to Eq. (A8) of the Appendix, the stretching ratios in the capillary entry region reached values up to several hundred in comparison to the maximum of 25 in the uniaxial elongation experiment. Considering the measurements of elongational flow from the barrel into the slit die as shortly addressed in the Appendix, elongational rates much higher than for the LDPE in the uniaxial experiments have to be dealt with for the entrance geometries used. Furthermore, shear rates and total shear for the extrusion of the polypropylenes through the capillaries of this paper are distinctly larger than in case of the shear of the LDPE in the parallel-plate rheometer. These differences do not explain the contrary results, however.

Rather the different time scales seem to play a decisive role. The high apparent shear rates applied in the capillary flow lead to short stretching and shearing times of the melt.

According to Eq. (A3), they range from several hundredths of a second at the highest shear rates to some tenths at the lowest and are distinctly shorter than the longest relaxation time of 400 s at 180 °C found for the LCB-PP pretreated in a



twin-screw extruder. From this simple consideration, it has to be concluded that a great deal of the pretreatment by the capillary flow applied takes place in the elastic regime of deformation. Thus, it has to be assumed that most of the molecules are not able to disentangle, but the entanglement network is deformed during the pretreatment. Obviously, this state seems to be very stable in case of the long-chain branched molecules, because for the LCB-PP extruded through capillaries at high shear rates a distinct pretreatment effect on the extrudate swell measured subsequently at a low stress in the melt indexer is found. The topological change postulated leaves the branching structure intact as shown by the molecular characterization in the highly diluted state of Fig. 3.

## Conclusions

The decrease of elastic properties by a mechanical pretreatment of the studied LCB-PP in a capillary rheometer, which was characterized by extrudate swell at a low shear stress, cannot be related to a change of the radius of gyration of the long-chain branched polymer that was found to remain unchanged by the pretreatment. This means that the length and distribution of the branches are not affected.

The decrease of the high molar mass component of the sample found according to the mechanical pretreatment can be excluded as the molecular reason for the reduction of the extrudate swell of the LCB-PP, because a purely thermally induced degradation of the high molar masses did not change extrudate swell.

From this finding, it can be concluded that the extrudate swell of the LCB-PP is strongly related to the long-chain branching structure.

Thus, a modification of interactions between branches due to the pretreatment applied is postulated as the source of the decrease in extrudate swell. A simple assumption can be used for making such an effect plausible. As proposed by Münstedt (1981) and taken up by Leblans and Bastiaansen (1989), branches and in particular the outer parts of a tree-like structure with higher mobility may get aligned to each other by the mechanical treatment. Thus, the whole ensemble approaches the conformation of linear molecules, the elastic effects of which are known to be smaller than those of conformations of long-chain branched molecules in their equilibrium state.

However, this coarse model does not explain the finding of the modification being stronger by the shear than the elongation exerted on the melt during capillary flow.

Thus, the given qualitative interpretation may be considered as a first step, only, to explain the mechanical pretreatment effect of long-chain branched polymers. A model for a deeper understanding is still missing.

## Appendix. Basic relations of capillary flow

For a Newtonian fluid, the profile of the shear rate in a circular capillary is linear. The shear rate  $\dot{\gamma}$  is zero in the center of the capillary and reaches its maximum at the wall, which follows as

$$\dot{\gamma} = 4\dot{V}/\pi R^3 \quad (\text{A1})$$

with  $\dot{V}$  being the volume rate or throughput and  $R$  the radius of the capillary. For a non-Newtonian melt, the shear rate along the capillary radius is not linear any longer and Eq. (A1) then stands for the apparent shear rate  $\dot{\gamma}_a$ .

The volume rate follows as

$$\dot{V} = \pi R^2 v \quad (\text{A2})$$

with  $v$  being a mean velocity of the melt in the capillary. From the length  $L$  of the capillary, a characteristic throughput time

$$t = L/v = \frac{4L}{R\dot{\gamma}_a} \quad (\text{A3})$$

can be determined.

More complex is the elongational flow in the entrance region. It is well known that secondary flow patterns may occur, in particular for long-chain branched polymers as described in the literature. Using laser-Doppler velocimetry, it was possible to obtain a deeper insight into entrance flow (Wassner et al. (1999)). Some of the results with relevance to mechanical pretreatment effects by capillary entrance flow are shortly addressed. For example, elongations, elongation rates, and time scales occurring in special flow geometries at various throughputs are of interest.

Wassner et al. (1999) studied the flow of an LDPE from a reservoir with a squared cross section of 14 mm × 14 mm into a slit of 14 mm in width and 1 mm in height at several apparent shear rates. Velocity profiles and following from them elongational rates  $\dot{\epsilon}$  along the central axis of the reservoir were measured. For the largest applied apparent shear rate  $\dot{\gamma}_a = 182 \text{ s}^{-1}$ , the elongational rate  $\dot{\epsilon}_{\max} = 22 \text{ s}^{-1}$  was found. Furthermore, it was shown that a master curve could be established by plotting  $\dot{\epsilon}\dot{\gamma}_a$  as a function of the normalized time  $t\dot{\gamma}_a$ . From this result, it can be derived that compared to the laboratory rheometer, much higher elongational rates may be expected in the narrowing ducts of the capillary rheometer used for the mechanical pretreatment at the shear rates up to  $14,400 \text{ s}^{-1}$ .

However, in parallel to increasing shear rates, the throughput times and the times for flow of the melt through the reservoir decrease. Thus, the total elongation is restricted, and it was determined from the flow profile to be close to the ratio of the side length of the quadratic reservoir to the slit height in accordance with the following simple geometric considerations.

Assuming an undisturbed flow field, for incompressible fluids like polymer melts, the volume of an element in the reservoir with the cross section  $A_r$  and the length  $L_r$  remains the same when stretched to the length  $L_c$  and the cross section  $A_c$  of the capillary, i.e.

$$A_r L_r = A_c L_c \quad (\text{A4})$$

and the stretching ratio  $\lambda$  follows as

$$\lambda = L_c/L_r = A_r/A_c \quad (\text{A5})$$

By differentiation of the lengths with respect to time one obtains the ratios of the velocities

$$v_c = dL_c/dt = A_r/A_c dL_r/dt = A_r/A_c v_r \quad (\text{A6})$$

or

$$v_c/v_r = A_r/A_c = \lambda \quad (\text{A7})$$

In the studies mentioned above, the cross section of the slit was  $W \times H$  and that of the reservoir  $W^2$ . Thus, the stretching ratio follows as  $W/H$ . Although these results were obtained for a slit die and a reservoir with a quadratic cross section, it is assumed that they can be used at least qualitatively for the discussion of the studies in this paper on the pretreatment effects in extrusion devices with circular geometries, for which the stretching ratio becomes

$$\lambda = r_r^2/r_c^2 \quad (\text{A8})$$

where  $r_r$  and  $r_c$  are the radius of the reservoir and the capillary, respectively.

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## Declarations

**Conflict of interest** The authors declare no competing interests.

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