RESEARCH ARTICLE

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Correlations of single-point parameters of linear rheology and molecular weight distribution of polypropylene homo- and copolymers

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Abstract

For various purposes, it is required to compress the shape of the molecular weight distribution (MWD) of polymers into a limited set of parameters. With increasing molecular weight and polydispersity, the MWD data obtained from chromatography become increasingly unreliable due to deficiencies in the high molecular weight region, making estimation via melt rheology more preferable. A number of empirical parameters obtained from melt rheology can be related back to MWD parameters. The target of this study is to establish the reliability of such relations for polypropylene homo- and copolymers. It is found that correlations between polydispersity from rheological crossover modulus and polydispersity via chromatography are not always valid. Therefore, the range of applicability must be kept in mind when attempting predictions based on these correlations because rheological measurements are sensitive to molecular characteristics in ways different from chromatography. The use of a modified polydispersity index is shown to be more reliable.

KEYWORDS
molecular weight, parameter correlations, polydispersity, polypropylene, rheology

1 | INTRODUCTION

The rheological behavior of thermoplastic polymers, which is critical both in polymerization and conversion, results from a combination of chain structure (chemistry and stereostructure), chain topology (branching degree and branch length), and molecular weight distribution (MWD).[1–18] Although modeling efforts have been made for all of these aspects and different rheological approaches, the highest number of papers deals with establishing models for interrelating the linear viscoelastic behavior and MWD of linear (non-branched) polymers.[3–7,9,10] Over time, various factors have renewed the interest in this interrelation; ranging from fundamental understanding of polymer

molecules behaviors[9,10,19] through the design of target MWD for specific processes[8,13,17,20] and applications, to the use in advanced flow modeling and production simulation.[15] A specific aspect in the industrially very relevant area of polyolefins has been the use of dynamic rheology instead of high temperature size exclusion chromatography for determining MWD or MWD-related parameters to be used in polymer design and production control.[6,15] Although high-temperature gel permeation chromatography (HT-GPC) gives very detailed information[21] and can be coupled with other methods for getting additional information about the composition of the polymer, like comonomer content or branching,[22] it requires extensive calibration and suffers from poor interlaboratory

comparability.[23,24] In contrast, melt rheology has been proven to be highly reproducible in round-robin tests involving both industrial and academic laboratories.[25,26] A high number of studies for relating rheology to MWD exists for isotactic polypropylene (iPP) homo- and copolymers.[8,27–48] Like polyethylene (PE), PP is normally characterized by a broad MWD and a high polydispersity as expressed by the ratio between mass and number average molecular weight, M_w/M_n. This results in a typically "soft" form of the corresponding storage and loss modulus, G' and G'', as a function of frequency, ω, of which only a limited frequency range is easily accessible. Using time–temperature superposition[19] for expanding said range is also of limited value because the respective shift factors are rather small due to the large distance between the usual measuring range of 180–240°C and the glass transition of ∼0°C. Full MWD calculations from dynamic moduli, as performed in the group of Friedrich[4,6,7] for polystyrene (PS) are consequently difficult for PP, and deviations found can mostly be linked to said narrow frequency range.[7,37] Morshedian et al. investigated the rheology and associated MWD of five commercial isotactic PP grades, employing a rheological material function to predict the MWD data. They highlighted the high sensitivity on the presence of low amounts of high molecular weight fraction, which was strongly affecting rheology but not GPC.[49] Varshouee et al proposed a mathematical model to link basic polymerization process parameters with the M_w and melt flow rate (MFR) as key polymer design parameters for polypropylene. The model outputs are in agreement with experimental results for an initial estimation, however the MFR corresponds to a single frequency of the whole rheological measurement scale, possibly missing parts of the complete picture.[50] Further problems appear when extending considerations into iPP copolymers, especially heterophasic (impact) copolymers with a multiphase structure.[51] The rheology of these materials comprising a iPP homo- or random copolymer matrix and a disperse phase of predominantly amorphous ethylene-propylene copolymer (EPC) is rather complex, contributions coming from both phases, plus also the interface as a function of particle size and compatibility.[45,52,53] The fact that papers including both homo- and copolymers in their respective analysis find deviations between the material classes[41,42,48] is thus not a surprise, but a logical expectation.

A full interconversion between rheology and MWD is, however, not always necessary. For the purpose of quality control (QC),[5,8] trend prediction[13,16,17,54] or the definition of parameters for patents, the calculation of single-point parameters correlating to M_w, M_w/M_n or higher moments of the MWD, like the ratio of z-average, M_z/M_w, is often sufficient. In industrial production, monitoring the MFR is still a standard measure of on- and off-line QC. Even in cases where online rheometers are

in use, those are often limited to high shear rates.[55,56] While on-line results can be correlated to the behavior in standard off-line capillary rheometers and injection molding,[57] they are of limited value for polydispersity calculation. Dynamic off-line rheometry has therefore been established as QC method, and the frequency range is kept narrow to accelerate the procedure. Single-point parameters based on these data facilitate operation.

One option is by using the crossover-point of the dynamic moduli

$$G'(\omega_c) = G''(\omega_c) = G_c, \tag{1}$$

where the parameters of crossover frequency ω_c and polydispersity index PI are defined as

$$PI = \frac{10^5}{G_c}. \tag{2}$$

The G_c is commonly related to M_w and the PI to M_w/M_n as suggested first by Zeichner and Patel,[29] and elaborated in numerous other papers.[30–33,36,39–42] Limitations of this approach have been pointed out,[38] but can mostly be related to polymer type and composition.[41,42,48]

An alternative type of polydispersity index is based on the MODSEP parameter (for "modulus separation"), introduced by Yoo[34] for high-MFR or low molecular weight PP, for which the crossover point is outside the normal measuring range:

$$MODSEP = \frac{\omega(G' = 10^4\,Pa)}{\omega(G'' = 10^4\,Pa)}. \tag{3}$$

The modulus level in Equation 3 has been selected rather arbitrarily over time by others, adapting it to available datasets. A value of 500 Pa is used in patents of LyondellBasell[58–61] in combination with the following PI definition:

$$PI_{MS} = 54.6 \cdot MODSEP^{-1.76}. \tag{4}$$

The factor and exponent have been selected in order to make the result similar to the conventional PI level. This Equation 4 is used in the present study. A third and purely empirical polydispersity measure used commonly inside Borealis is the 'shear thinning index' SHI.[8] Here, similar to MODSEP, the complex viscosity η^* at different levels of complex modulus G^* is defined as

$$G^* = \sqrt{G'^2 + G''^2} \text{ and } \eta^* = \frac{G^*}{\omega}, \tag{5}$$

with the actual parameter being

$$SHI\left(\frac{a}{b}\right) = \frac{\eta^*(G^* = a\,kPa)}{\eta^*(G^* = b\,kPa)}. \tag{6}$$

If $a = 0$ in this equation, then the SHI is related to η_0. For the present study, α was chosen as 3 and b as 50 $\alpha\nu\delta$ 100, giving the SHI(3/50) and SHI(3/100) parameters, respectively.

The most logical alternative to ω_c as parameter related to M_w is the zero shear viscosity η_0, the Newtonian limit of the viscosity curve at low shear rates or low frequencies. Validity of the Cox-Merz relation,

$$\eta^*(\omega) = \eta(\dot{\gamma}), \text{with } \omega = \dot{\gamma}, \tag{7}$$

is assumed for the present study. Adapting the Mark–Houwink equation,[1,2,8,19] one arrives at the well-known relation:

$$\eta_0 = kM_w^a, \text{ with } a = 3.2 - 3.6. \tag{8}$$

We used rather large datasets of MWD and dynamic rheology of PP homo- and copolymers coming from one laboratory in order to test the various correlations. The target was to check for differences in terms of validity and prediction power of the different parameters discussed.

2 | EXPERIMENTAL

2.1 | Materials

Linear polypropylenes of different molecular architectures were considered for this study, both homo- and copolymers from commercial or pilot-scale production and based on Ziegler–Natta catalysts systems. Polypropylene homopolymers (PPH) comprising propylene as monomer and random polypropylene copolymers (RACO) with ethylene as comonomer are both single-phase materials. Heterophasic copolymers and random-heterophasic copolymers (RAHECO) consist of a crystalline polypropylene homo- or copolymer matrix with amorphous EPC inclusions.[62,63] For the production of the RAHECOs, in the first step a crystalline random copolymer is produced and in the next step the rubbery phase is copolymerized in another reactor, the resulting products being normally softer than the other grades.[64] In Tables S1–S4 the respective results of the GPC and rheology measurements of polymers used in this work are listed, as well as calculated parameters. The polymers were provided by Borealis AG and were used as received (i.e., containing standard additives like antioxidants, acid scavengers, and in some cases nucleating and/or antistatic agents). All differences in the molecular architecture of the materials are associated with the production process and catalyst used.

2.2 | Rheology

The rheological measurements were carried out according to ISO 6271-1 and 6271-–10, using an Anton Paar MCR 501-CTD450 and MCR 301 rheometer, each equipped with a convection oven. The measurements were performed under nitrogen atmosphere to prevent oxygen-induced chemical reactions, such as oxidation and degradation. Parallel plate-plate geometry was used, with plates of 25 mm in diameter. The frequency range was from 628 to 0.01 rad s^{-1} with a five points averaging per decade. The applied strain was 2% to 7%, distributed in a logarithmic ramp to the amount of data points to stay within the linear viscoelastic regime and to achieve a good signal to noise rate of the instrument. A gap between 1.3 and 0.6 mm was used, depending on the materials' viscosity behavior. If the test material showed low viscosity behavior, the gap was reduced stepwise to achieve a well-filled gap without material leakage. All measurements were carried out at 200°C. Both zero shear viscosity (η_0), crossover-related measures (ω_c, $1/G_c$), and empirical parameters (SHI and PIMS) were obtained. The viscosity curves are shown in Figure S1.
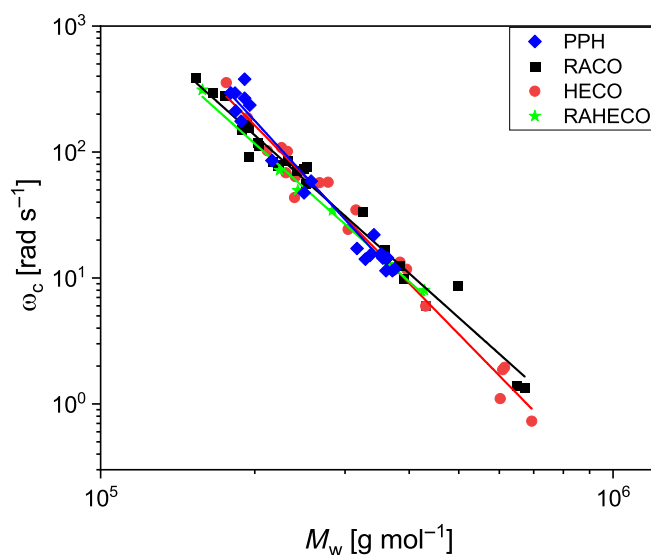
2.3 | Gel permeation chromatography

For the measurement of the molecular weight and the MWD, a polymer char HT-GPC instrument, equipped with an IR5 (four-band infrared detector) was used. The separation took place on one Agilent-PLgel Olexis guard column and three Agilent-PLgel Olexis columns. The samples were dissolved in 1,2,4-trichlorobenzene stabilized with 250 mg L^{-1} 2,6-di-tert-butyl-4-methyl-phenol. The same solvent with the same amount of stabilizer was used as mobile phase. The temperature of the system was kept constant at 160°C and the flow rate was 1 mL min^{-1}. For each analysis, a volume of around 200 μL was injected. The calibration of the column set was done by universal calibration with narrow molecular weight PS (0.5–11,500 kg mol^{-1}). The Mark–Houwink constant for PS, PE, and PP was given by ASTM D6474-99. All samples were prepared by dissolving 5.0 to 9.0 mg of polymer in 8 mL in the mentioned solvent at 160°C during gentle shaking on the auto sampler of the HT-GPC instrument.[62,65] Out of the GPC measurements, weight average molecular weight M_w and the broadness relations M_w/M_n, and M_z/M_w were obtained as characteristic parameters. The GPC curves are shown in Figure S2.

3 | RESULTS AND DISCUSSION

Figure 1 depicts the correlation between ω_c and M_w. The frequency where flow starts is related to the end-to-end relaxation and is strongly dependent on the molecular weight. The correlation can be approximated by a linear fit, and the corresponding parameters are summarized in Table 1. The validity of the correlation described in Section 1 can be verified. Although not ideal, it should be noticed that its validity depends heavily on the MWD of the materials. Despite the different polymer architectures included, the slopes are in the same range, and the correlation coefficient R^2 is very high. The slope of the copolymers is higher than the prediction for PPH.[41] Therefore, to estimate the M_w from ω_c available by rheology data, always the equation of the respected PP type must be known and used.

For the materials where the Newtonian plateau was reached, and thus, the determination of the zero shear viscosity was possible. The respective values, covering almost four orders of magnitude, are plotted against weight average molecular weight in Figure 2. The data are again fitted with a linear equation, and the resulting fit parameters are listed in Table 2. The slopes are in the same range and lay between 3.8 and 4.4, somewhat higher than the prediction of 3.4.[8] This range is also reported by previous investigations.[4,8] The precision is very good with a resulting R^2 of >0.96. The deviation observed for some samples most probably arises from the difficulty to estimate η_0 in cases where η is far from reaching a plateau at low frequencies in the rheology experiment, thus, making the extrapolation to zero shear less accurate.

In Figure 3, the PI calculated with a rheological model (Equation 2)[41] is plotted against the MWD broadness measured by GPC. The black line has a slope of 1. According to the literature,[29] a correlation of these parameters with a slope of 1 exists. However, no clear linear correlation was identified for these PP types. For the RACO, an approximate linear dependence can be seen,

FIGURE 1 Dependence of ω_c on the total molecular weight. The lines are linear fits to the data. [Color figure can be viewed at wileyonlinelibrary.com]
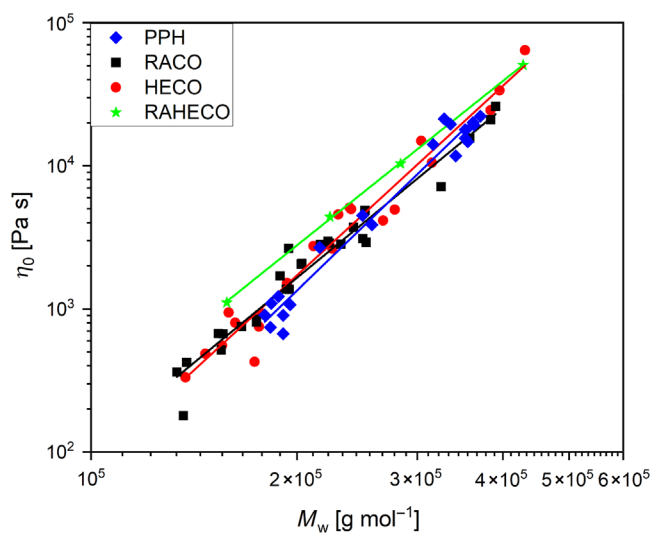

FIGURE 2 Dependence of η_0 on the total molecular weight. The lines are the result of linear fit to the data. [Color figure can be viewed at wileyonlinelibrary.com]

TABLE 1 Results of the linear fit of Figure 1.

	Slope	Intercept[rad s^{-1}]	R^2
PPH	−4.4 ± 0.2	25.8 ± 0.9	0.97
HECO	−4.2 ± 0.1	24.3 ± 0.8	0.98
RACO	−3.6 ± 0.1	21.4 ± 0.6	0.98
RAHECO	−3.6 ± 0.1	21.3 ± 0.8	0.99

Abbreviations: HECO, heterophasic copolymers; RACO, random polypropylene copolymers; RAHECO, random-heterophasic copolymers; PPH, polypropylene homopolymers.

TABLE 2 Results of the linear fit of Figure 2.

	Slope	Intercept [Pa s]	R^2
PPH	4.6 ± 0.2	−21 ± 1	0.97
HECO	4.4 ± 0.2	−20 ± 1	0.96
RACO	3.9 ± 0.2	−17.7 ± 0.8	0.96
RAHECO	3.8 ± 0.4	−16.8 ± 0.2	0.99

Abbreviations: HECO, heterophasic copolymers; RACO, random polypropylene copolymers; RAHECO, random-heterophasic copolymers; PPH, polypropylene homopolymers.
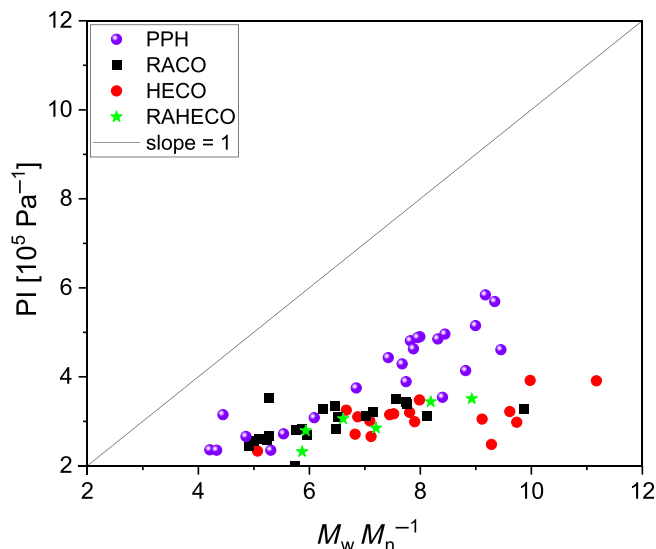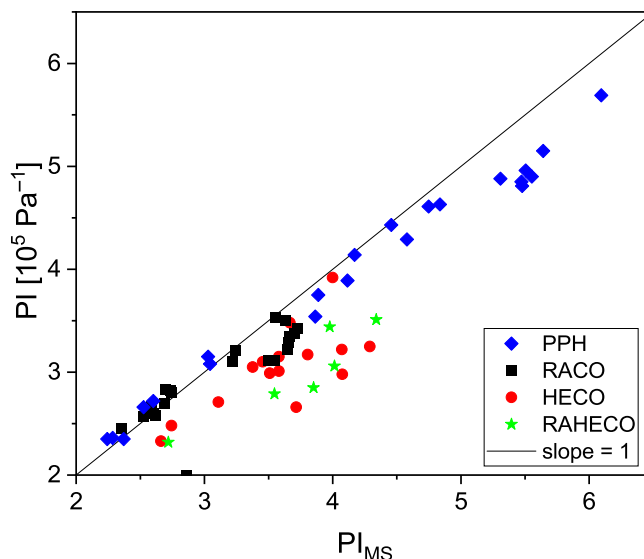
FIGURE 3 Dependence of PI calculated from G_c on polydispersity measured by GPC. The high molecular weight tail makes the direct comparison of the parameters particularly difficult. [Color figure can be viewed at wileyonlinelibrary.com]

FIGURE 4 Correlation of the rheological measured parameters PI and PI_{MS}. [Color figure can be viewed at wileyonlinelibrary.com]

but the slope of a linear fit would differ significantly from unity. Therefore, the scalability of these results is questionable. This could be attributed to the high molecular weight tail, which does not contribute significantly to the calculated PI. Therefore, the prediction of the molar mass (Figure 1) is more reasonable than the prediction of PI.

In Figure 4, the correlation of the PI calculated via the G_c and the PI_{MS} is shown, including a line with a slope of 1. The data of PPH follow that line closely, but for the rest there is no linearity. This means that the parameters PI and PI_{MS} are not scalable. This could be a proof that the PI_{MS} parameters do not fit for these types of polymers. A different prefactor and exponent in Equation 4 could possibly yield a better fit with a slope of 1. Moreover, performing this evaluation at another level of G' and G'' could yield better results.

In Figure 5, the shear thinning indices SHI(3/50) and SHI(3/100) as a function of polydispersity are depicted. By considering the scale of the figures, the range of the values of SHI(3/100) is much higher than the values of SHI(3/50). Although both indices exhibit an increase on increasing MWD broadness, there are several samples with an SHI deviating from the general trend. The apparent better correlation for the SHI(3/50) is a result of the lower value and scatter of this parameter. A linear fit of this data would make no sense due to the broad scattering of data points.

It can be observed that for all the investigated materials there is a linear correlation between the crossover frequency ω_c and the weight average molecular weight M_w, as well as between the zero shear viscosity η_0, and

the weight average molecular weight M_w. This means that if a linear fit of the same product type is known, the M_w can be estimated. It is important to differentiate between the polypropylene types: There is no universal fit, which would be applied to all PP types, that is, combining homopolymers and copolymers. The same is valid for the relation between ω_c and M_w.

For all other parameters, no linear correlation was found. Most surprising was the finding for the PI calculated from the crossover modulus G_c versus $M_w M_n^{-1}$ measured by GPC. Zeichner and Patel had shown this correlation in a publication with a slope of around 1 and a very high R^2.[29] It is assumed that they used very homogenous product types, which had all been produced in the same way. As seen in Figure 3, the data points of the present work are all far away from the line with a slope of 1, and the correlations are much flatter. Therefore, this relation should not be used to compare different polymer parameters. One reason might be that with increasing molecular weight and polydispersity, the MWD data obtained from SEC become increasingly unreliable due to detector signal deficiencies in the high molecular weight region. This is true, though mostly for conventional GPC analysis where only a concentration detector is use that is, refractometer or IR. The use of GPC-LS provides more reliable results for the determination of polymers of very high M_w and M_z.

Finally, one of the discussed empirical parameters is the PI_{MS}. As seen in Figure 4, the data points are scattered. No linearity is detected, except for the RACO.
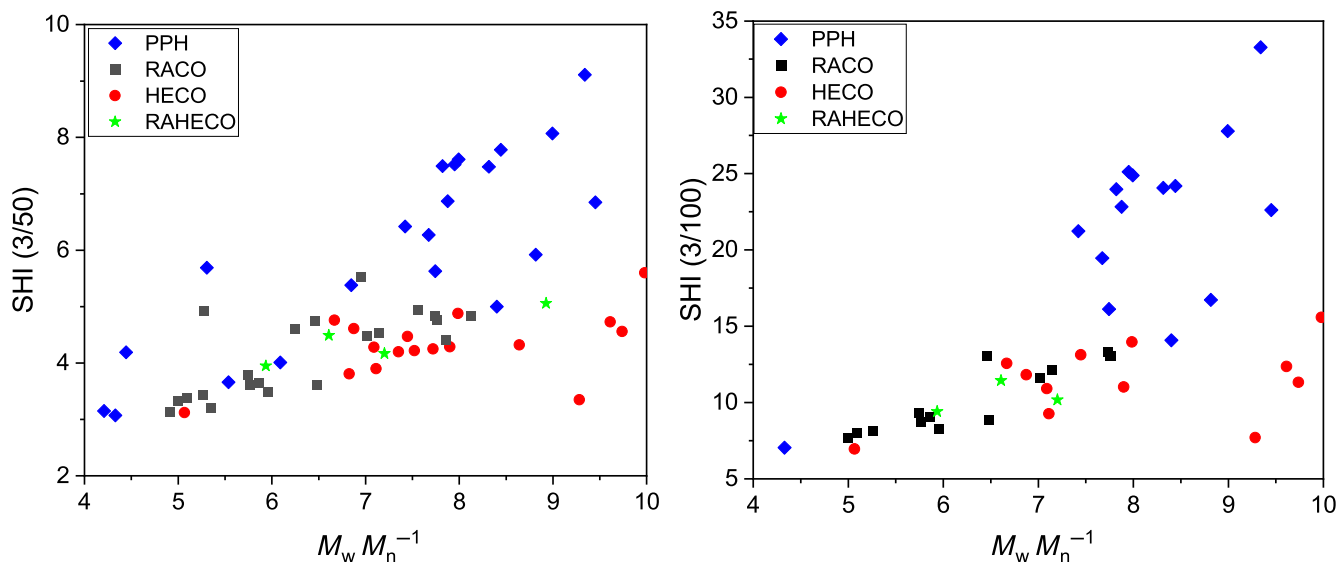
FIGURE 5 SHI(3/50) (left) and SHI(3/100) (right) as a function of polydispersity. [Color figure can be viewed at wileyonlinelibrary.com]

Nevertheless, the slope of a linear fit of the RACO is estimated to 0.66. Therefore, the scalability of these parameters is questionable. It is possible that for other polymers this formula works well, but for PP a different prefactor and exponent might be more appropriate. This is in agreement with the case of ultrahigh molecular weight PP studied by Ianniello et al.,[66] for determining the MWD of blends through rheology experiments. They found a good potential in deriving such estimates by a mixing rule, but underline the strong dependence of accuracy on the average molecular weight.

The same can be said for the SHI values, which again show a general positive correlation to MWD broadness, but with an even bigger scattering tendency than PI and PI_{MS}.

4 | CONCLUSION

The relations between the rheological and GPC data can provide an insight into the molecular properties of polymers. Several rheological single-point parameters exist, many of the newer ones being of empirical origin. Nevertheless, some parameters can be useful for specific applications, like the usage of the SHI. Generally, the use of rheological methods for an estimation of the M_w in the high molecular region can be supported. In the case of polypropylenes of different chain architecture, ranging from homopolymers to copolymers, the range of applicability of such approximations is limited to low molecular weight distributions because rheological measurements are more sensitive to high molecular weight segments.

AUTHOR CONTRIBUTIONS

Georg Gschwendner: Data curation (lead); investigation (lead); visualization (equal); writing – original draft (equal). **Antonis Gitsas:** Supervision (lead); visualization (equal); writing – original draft (equal); writing – review and editing (lead). **Markus Gahleitner:** Conceptualization (lead); methodology (lead); supervision (equal); writing – original draft (lead); writing – review and editing (equal). **Patrick Moser:** Methodology (lead); writing – review and editing (supporting). **Christian Paulik:** Supervision (lead); writing – review and editing (supporting).

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SUPPORTING INFORMATION

Additional supporting information can be found online in the Supporting Information section at the end of this article.