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Characterization of long-chain branching effects in linear rheology

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Synopsis

This is the last part of a series of five articles published in Journal of Rheology (Maier et al. (1998), Thimm et al. (1999a), Thimm et al. (2000a), Thimm et al. (2000c)) in which progress on the determination of binary molecular weight distributions from rheological data has been reported. In this article is discussed in how far the developed methods can also be used to characterize long-chain branching effects.

Monomodal samples which contain long-chain branches will show two relaxation processes in the rheological examination, which are converted to two peaks in a corresponding molecular weight distribution. But these samples will show only one peak in a molecular weight distribution determined by a size-exclusion chromatography examination. This difference can be used to characterize long-chain branched materials as will be explained in this article.

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The usefulness of this method is demonstrated by examining polymers, which contain definite long-chain branches specified from the way, they were made.

I. Introduction

Thimm et al. (1999a, 1999b, 2000a, 2000b, 2000c) have shown recently, how the molecular weight distribution (MWD) of binary polymer blends made of monodisperse components of linear polymers can be reconstructed from rheological data. The quality of the reconstruction gave results comparable to a size-exclusion chromatography (SEC) determination of the molecular weight distribution, which is a well-established method.

A central key of their method is the determination of the relaxation time spectrum. While the relationship between the molecular weight distribution of linear polymers and the linear rheological properties is henceforth well understood, there is another problem in polymer characterization, where rheology might be useful. This is the examination of the relationship between long-chain branching effects and rheological properties. So far there is no method available to characterize long-chain branching in a robust and reliable manner. In this article we discuss how the relaxation time spectrum and the method developed by Thimm et al. (1999a, 2000a) can be used examining this problem.

For polymers with long-chain branches (armes), which are longer than the entanglement molecular weight ($M_e$), it is found, that the terminal relaxation time shifts with the arm length towards longer times. This shift corresponds to violation of the well-known 3.4 scaling law between molecular weight ($M_w$) and the zero shear rate viscosity $\eta_0$.

Furthermore, the relaxation time spectrum of long-chain branched materials shows two peaks corresponding to two relaxation processes. These can be interpreted as the processes corresponding to the relaxation of the arms and the relaxation of the whole molecule.
To clarify our notation, we name the molecular weight distribution, which was determined with size-exclusion chromatography 'size-exclusion chromatography determined molecular weight distribution' (sMWD), while the molecular weight distribution determined from rheological data is named 'rheological molecular weight distribution' (rMWD). The difference between rMWD and sMWD will be called 'difference molecular weight distribution' (dMWD). In this article will be discussed that this dMWD can be reasonably interpreted as molecular weight distribution of the branches (arms).

While the rheological relaxation processes are well reflected in the relaxation time spectrum, the size-exclusion chromatography can not differentiate these processes. Therefore, there is just one peak in a size-exclusion chromatography determination of the sMWD from a monomodale long-chain branched polymer sample. On the other hand one finds a binary distribution, in the rMWD, since there are two relaxation processes. These differences therefore report, whether a sample contains long-chain branches or not.

The two peaks in the rheological rMWD are explained on a phenomenological level in this article. We take the picture as guideline that the shorter relaxation processes in the relaxation time spectra correspond to the relaxation of the arms, while the longer relaxation processes correspond to the relaxation of the whole polymers. Then it seems plausible that the shorter relaxation processes, when converted to a molecular weight distribution, tell the polydispersity and length of the branches, while the peak at higher relaxation times corresponds to the relaxation of the polymer. It is plausible that the peak might be found at higher molecular weight than would be determined with the size-exclusion chromatography, since the branches prevent reptation and this can lead to slower relaxation.

The method itself is described in section II. In section III. results found for specially designed H-shaped molecules are discussed. In section IV. we discuss, in how far these results can be transferred to polyolefines. In section V. the conclusions are given. Finally, in the appendix the relation between the results
obtained using the novel method to established theoretical work on long-chain branching in polymers is discussed.

In the remaining subsection of this introduction we briefly reflect on the method introduced by Thimm et al. (1999a, 2000a) to convert the relaxation time spectrum into a rheological molecular weight distribution.

**Relaxation time spectrum and molecular weight distribution**

Thimm et al. (1999a) derived some analytical relations, which relate the relaxation time spectrum \( h(\tau) = \tilde{h}(m) \) (with \( \tau = \tau(m) \)) to the molecular weight distribution \( w(m) \) for linear polymers. The rheological molecular weight distribution is given by:

\[
w(m) = \frac{1}{\beta} \frac{\alpha^{(1/\beta)}}{(G_0^0)^{1/\beta}} \tilde{h}(m) \left( \int_m^\infty \frac{\tilde{h}(m')}{m'} \, dm' \right)^{(1/\beta - 1)},
\]

and the inverse relation is given by:

\[
\frac{\tilde{h}(m)}{G_0^0} = \frac{\beta}{\alpha} w(m) \left[ \int_m^\infty \frac{w(m')}{m'} \, dm' \right] \beta^{-1}.
\]

In these equations the generalized mixing parameter is about two \( (\beta = 2) \), when the Rouse spectrum is treated separately in the data evaluation (Thimm et al. (2000a)). The plateau modulus is denoted \( G_0^0 \). On the one hand these relationships are especially useful to understand rheological data from binary molecular weight distributions. On the other hand, this knowledge can be used to compare the results of rheological measurements to these obtained with size-exclusion chromatography. However in addition to the conventional determined rheological data (dynamic shear moduli, creep function) the constants \( k, \alpha \approx 3.4 \) in the scaling relation

\[
\tau = km^\alpha,
\]

where \( \tau \) is a relaxation time and \( m \) a normalized molecular weight, have to be determined experimentally.
II. The method

In this section the novel method is introduced. To use this method, the following quantities have to be determined:

(i) The relaxation time spectrum \( h(\tau) \) has to be estimated from measured rheological data (e.g. shifted dynamic moduli \( G'(\omega), G''(\omega) \)). (How this estimate can be obtained is described e.g. in Roths et al. (2000).)

(ii) The 'size-exclusion chromatography determined molecular weight distribution' should be measured experimentally.

We make the following assumptions (if the parameters are not known from different experimental determinations) concerning the parameters, which are needed to calculate the molecular weight distribution.

(iii) For the value of the generalized mixing parameter \( \beta \) we set the theoretical value \( \beta = 2 \).

(iv) For the scaling parameter \( \alpha \) we set the universal value \( \alpha = 3.4 \).

With these parameters fixed there are two additional 'free' parameters left, which have still to be determined. This determination is an essential non-trivial step in this method.

(v) The time where the Rouse spectrum vanishes (named \( \tau_R \) in Thimm et al. (2000a)) can be accurately determined using the following idea:

When \( \tau_R \) was determined wrongly, there would be a discontinuity in the rheologically determined molecular weight distribution at the position corresponding to \( \tau_R \). Therefore, we take the value for \( \tau_R \), which guarantees a smooth rheological molecular weight distribution in the region between the determined \( \tau(m_e) \) and the terminal relaxation time.
(vi) A well-established observation is that the value $k$ in the given scaling relation Eq. (3) depends strongly on the temperature and the molecular weight of the branches (arms) (see appendix).

Therefore, it is not possible to use constant literature values or values determined from linear polymers to determine $k$. The result of such a use would be that the peak corresponding to the sMWD would be found at molecular weights, which are too high. Also the use of a different theoretical scaling relation would be of little help, since for a branched polymer sample of unknown topology the details in these relations would differ strongly.

To be able to reasonably combine sMWD and rMWD, we suggest to determine the terminal relaxation time $\tau_{\text{term}}$, which shows as terminal relaxation peak in the relaxation time spectrum. The position of this peak is for linear polymers related to the maximum in the SEC determined molecular weight distribution $m_{\text{term}}$. When both parameters are well determined, it is possible (inserting both values in Eq. (3)) to calculate $k$ accurately.

The $k$, which is determined this way is not the microscopic $k$, describing the properties of the tube in the reptation picture (Doi and Edwards (1986)), discussed above. However, as will be discussed below, the typical error, which will be made using this procedure, is acceptable and the procedure will give reasonable values for the arm molecular weight $M_{\text{arm}}$.

The practical realization of this thought could be to calculate in a first step the rMWD with an essentially arbitrary $k$ (for example the $k$ of linear polystyrene). In a second step the rMWD could be scaled such that the peak with the higher molecular weight matches the peak in the sMWD.

With the steps i) to vi) all is known needed to determine the rheological molecular weight distribution from the estimated relaxation time spectrum - using the procedure given in Thimm et al. (1999a, 2000a).
As outlined in the introduction, for a monomodal sMWD the rMWD is also monomodal for a sample without long-chain branches, but is binary for a sample containing long-chain branches.

The peak corresponding to the higher molecular weight is related to the relaxation of the whole molecule.

(vii) Therefore, we drop the peak corresponding to the higher molecular weight. This drop corresponds in general to build the difference between the rheologically determined molecular weight distribution with the molecular weight distribution determined with SEC.

(viii) The peak corresponding to the lower molecular weight reflects the molecular weight distribution of the long-chain branches (arms) and therefore characterizes long-chain branching effects in polymers.

A parameter, which could be used for quantitative comparison, could be the average of the dMWD. We name this average $M_{arm}$ and discuss in the following subsection, that this average will be of the same order, as would be expected for the microscopic $M_{arm}$.

**Typical values**

To give a feeling for typical values for $M_{arm}$, which can be expected using this method, we discuss some simple considerations in this subsection. We are interested in typical values, which are expected for $M_{arm}$, when $M_{term}$ is given by determination of sMWD.

The most simple argument is that obviously the following inequality must hold:

$$M_e < M_{arm} < M_{term}. \quad (4)$$

From topological considerations (the 3 arm star is the most simple branched molecule) it is clear that $M_{arm} < 1/3M_{term}$. Typically the reptation starts at
the critical molecular weight $M_c$, which is about a factor 2 greater than the entanglement molecular weight. To show effects the arm molecular weight should therefore be at least of this order $2M_e < M_{\text{arm}}$. When we consider the value for $M_{\text{term}}$ of $M_{\text{term}} \approx 1\text{Mio.g/mol}$, and the typical value for the entanglement molecular weight $M_e \approx 10000\text{g/mol}$, we find approximately that:

$$1/50 M_{\text{term}} < M_{\text{arm}} < 1/3 M_{\text{term}}.$$  \hspace{1cm} (5)

So a determination of the arm molecular weight using rheological means by given $M_{\text{term}}$ is obviously restricted to arms length within one decade.

Another consideration is that one may insert the scaling relations Eq. (3) for $M_{\text{term}}$ and $M_{\text{arm}}$ into each other. One finds easily:

$$M_{\text{arm}} = \left(\frac{\tau_{\text{arm}}}{\tau_{\text{term}}}\right)^{1/\alpha} M_{\text{term}}.$$ \hspace{1cm} (6)

We take for the ratio of $\tau_{\text{arm}}$ and $\tau_{\text{term}}$ the typical values 100 to $10^6$. The value 100 should be assumed to distinguish binary behaviour and the value $10^6$ represents the typical limits of the frequency window, which is accessible using rheology. When we insert these values together with the assumed scaling parameter $\alpha \approx 3.4$ we find the approximate values:

$$1/60 M_{\text{term}} < M_{\text{arm}} < 1/4 M_{\text{term}}.$$ \hspace{1cm} (7)

Both appraisements give for $M_{\text{arm}}$ a typical value of about $1/10 M_{\text{term}}$.

\textbf{III. Data evaluation}

In this section data from well-defined H-shaped polymers are examined. The data from the shifted dynamic moduli $G'(\omega)$, $G''(\omega)$ used, are given and discussed in (Roovers (1984), McLeish et al. (1999)). Moreover the original SEC-curves, provided generously by J. Roovers, were checked to confirm the result that the SEC-curves showed indeed just one peak.
A. Polystyrene

In this section we discuss results found for specially designed H-shaped polystyrene (Roovers (1984)).

Roovers (1984) has constructed three samples of perfectly designed H-shaped molecules where the molecular weight of the arms and the bar are the same. The ones we discuss in this article are named H2A1 ($M_w = 2.37 \cdot 10^5$ g/mol), H1A1 ($M_w = 4.83 \cdot 10^5$ g/mol) and H5A1 ($M_w = 10.4 \cdot 10^5$ g/mol). The weights for the arms can be obtained by division $M_w/5$. These were examined rheologically and later two groups have found that these rheological data contained indeed two relaxation processes (Friedrich et al. (1995), Hatzikiriakos et al. (2000)). The first group used a very stable analytical ansatz designed to find two relaxation processes in rheological data, while the second group found the analogous result using a discrete relaxation time spectrum.

The scaling parameters of linear polystyrene are determined experimentally (Maier et al. (1998)) to $k = 6.919 \cdot 10^{-20}$ sec ($m$ given in g/mol) and $\alpha = 3.67$. We use these parameters, having in mind that the peaks of the averaged molecular weights and the relaxation time spectrum need not match in our evaluation. We calculate the relaxation time spectrum and determine the rheological molecular weight distributions. The results are shown in figures 1a)-c) together with the averaged molecular weight of the nearly monodisperse polystyrene given by Roovers (1984) for the whole molecule and the arms.

The results show that the idea that the molecular weights of the molecules and the arms are reflected well by the rheological determined molecular weight distribution (rMWD) seems plausible. The shift seems to become large just when the mass of the arms exceeds the entanglement molecular weight, which is known to be for polystyrene about $M_e = 18000$ g/mol. The agreement between rheologically determined weights and the weights given from SEC by Roovers is remarkable. It seems plausible that the polydispersity given in the figures
reflects the polydispersity of the linear polystyrene, which was used to construct the samples.

B. Polyisoprene

A theory, which describes the dynamics of H-polymers in greater detail was worked out and discussed by McLeish et al. (1999). However this group did not solve the ill-posed inverse problem to estimate the spectrum from the measured dynamic moduli.

McLeish et al. (1999) have examined and published data (in Fig. 6 of the cited article) of four H-polymers from polyisoprene. The samples are named: H110B20A ($M_w(SEC) = 198000\, \text{g/mol}, M_{arm}(SEC) = 20000\, \text{g/mol}$), H160B40A ($M_w(SEC) = 324000\, \text{g/mol}, M_{arm}(SEC) = 40000\, \text{g/mol}$), H110B52A ($M_w(SEC) = 310000\, \text{g/mol}, M_{arm}(SEC) = 52500\, \text{g/mol}$), H200B65A ($M_w(SEC) = 460000\, \text{g/mol}, M_{arm}(SEC) = 63000\, \text{g/mol}$).

The results for the rheological molecular weight distributions found with the 'step in' parameters for polystyrene are given in Fig.'s 2a)-d). The binary behaviour can be clearly identified. When the constant $k$ is determined as described above, the values are given in McLeish et al. (1999), the molecular weight distribution of the arms can be calculated with reasonable values comparing to the molecular weight averages for the arms given by McLeish et al. (1999). Results from the sample with the highest arm molecular weight are shown in Fig. 3.

We see in Fig. 2d), that it is important to check the validity of the procedure, that the frequency window, which is used to determine the rMWD, should be wide enough to contain two clearly separable peaks.

The agreement between the $M_{arm}$ given by construction and the $M_{arm}$ determined with the procedure proposed in this article seems to become better for the higher arm molecular weight. The same is observed for the polystyrene data.

A possible explanation for this observation could be that for the lower arm
molecular weight samples $M_{arm}$ is too close to the entanglement molecular weight $M_e$, to be well resolved. Below $M_e$, we assume the relaxation time spectrum to be dominated by the Rouse modes, while the influence of $M_{arm}$ should be vanishing in this region. For this reason it is also expected that the relaxation time spectrum should not reflect the microscopic molecular weight distribution of the arm molecular weight below $M_e$ correctly.

IV. Possible limitations concerning polyolefines

In this section results for an evaluation for various polyolefine samples (linear and branched) are summarized. (See also Friedrich et al. (1999), a more detailed evaluation will be published elsewhere.) Examining rheological data from polyolefines, we found binary behaviour of the rMWD in one sample (See Fig. 4). Taken the value of $k$ for polystyrene realistic values for $M_{term}$ and $M_{arm}$ are obtained. The rMWD shows indeed a broad peak in the rMWD, which can be interpreted as molecular weight distribution of the arms. The position of the peak is in good agreement with the theoretical considerations discussed in section II.

In general it is found that the binary behaviour is less clearly detectable than with the monodisperse H-shaped molecules of Roovers (1984). This observation can be motivated as follows:

(i) While the polystyrene samples contain nearly monodisperse ($M_w/M_n \approx 1.02$) parts, metallocene catalysts produce broader distributed polymers ($M_w/M_n \approx 2$). The broadening of the samples can be a reason that the binary behaviour is smeared out.

(ii) Since it is unclear how the long-chain branches in the samples are really distributed, it might be that the peak corresponding to the arm molecular weights is smeared out considerably, since the long-chain branches have very different lengths and positions.
(iii) The frequency windows of the (from dynamic moduli and creep curve constructed) mastercurves is limited. This limitation limits the mass range in which the rMWD can be accurately determined considerably as has been reported by Thimm et al. (2000b) for linear high density polyethylene. Therefore, the peaks of the corresponding binary molecular weight distributions may be outside the rheologically accessible frequency window.

Although the parameters for $k$ and $\alpha$ are essentially unknown for the new materials under consideration, the method described in this article can still give interesting information without essential limitations. The points discussed above are of technical manner, which are in principle not unsolvable. Therefore, these points do not question the idea of our novel approach.

V. Conclusion

For linear polymers the relationships between the molecular weight distribution and rheological data have been well examined (Thimm et al. (1999b, 2000a)). When the developed procedure is applied to branched polymers, we find that the rheologically determined molecular weight distribution can be reasonably interpreted as a reflection of the molecular weight distributions of the whole molecules and of the arms of the branched molecules.

Starting from this idea we have developed a novel method, which allows robust characterization of long-chain branching in polymers. This method is motivated on a phenomenological level.

Using this method, it is possible to explicitly determine the molecular weight distribution of the branches (arms), which is not accessible so far by any other method. We therefore think this method to be a valuable tool to characterize long-chain branching effects in polymers.
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Appendix: Connection to established theories

The influence of the quantity ’arm molecular weight’ $M_{arm}$ on various rheological quantities (like the zero-shear rate viscosity $\eta_0$, or the terminal relaxation time $\tau_{term}$) has been studied intensively in the literature (see e.g. Doi and Edwards (1986)). A well-known relationship (see e.g. Doi and Kuzuu (1980)) is the relation between the terminal relaxation time $\tau_{term}$ and the arm molecular weight $M_{arm}$ relative to the entanglement molecular weight $M_e$ and the corresponding relaxation time $\tau(m_e) = \tau_e$:

$$\tau_{term} = \tau_e \left( \frac{M_{arm}}{M_e} \right)^b \exp(\nu \frac{M_{arm}}{M_e}),$$ \hspace{1cm} (8)

where in good approximation one can take $\tau_{term} = \eta_0 / G_N$.

Once, $M_{arm}$ is determined with the new method ($M_{arm}$ is the average molecular weight of the arm molecular weight distribution), it is straightforward to insert $M_{arm}$ and these rheological quantities in the relations from literature. Solving such equations it is possible to estimate additional parameters (e.g. $b$ for given $\nu$), which are relevant in the theory of branched polymers.

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FIG. 1a
The rheologically determined molecular weight distribution for a H-shaped polystyrene sample (H2A1 in Roovers (1984)) . (Step-in parameters of linear polystyrene used).
FIG. 1b

The rheologically determined molecular weight distribution for a H-shaped polystyrene sample (H1A1 in Roovers (1984)).
FIG. 1c

The rheologically determined molecular weight distribution for a H-shaped polystyrene sample (H5A1 in Roovers (1984)).
FIG. 2a
The rheologically determined molecular weight distribution for a H-shaped polyisoprene sample. $G'(\omega)$, $G''(\omega)$ data taken from McLeish et al. (1999) (H110B20).
FIG. 2b
The rheologically determined molecular weight distribution for a H-shaped polyisoprene sample. $G'(\omega)$, $G''(\omega)$ data taken from McLeish et al. (1999) (H160B40A).
FIG. 2c
The rheologically determined molecular weight distribution for a H-shaped polyisoprene sample. $G'(\omega), G''(\omega)$ data taken from McLeish et al. (1999) (H110B52A).
FIG. 2d

The rheologically determined molecular weight distribution for a H-shaped polyisoprene sample. $G'(\omega), G''(\omega)$ data taken from McLeish et al. (1999) (H200H65A). The peak corresponding to higher molecular weight is incomplete due to limitations of the frequency range in the measured $G'(\omega), G''(\omega)$ data.
FIG. 3
The distribution of the arm molecular weight’s can be clearly identified using our novel procedure. The value for the average arm molecular weight is given by McLeish et al. (1999) as about 63000 g/mol.
FIG. 4

Examining data from polyolefines, we found a sample, which showed clearly binary behaviour.