CHAPTER I.3

CONCLUSIONS AND PERSPECTIVES

In the first place, in appendix II.1, we have developed a model to predict the linear viscoelasticity (LVE) of linear polymer melts. Based on the Time – Dependent – Diffusion des Cloizeaux [51] kernel and on the double reptation concept [52], and proposing a new expression to describe the Rouse relaxation, this model gives very good results for a wide range of samples. Its predictions were compared with those obtained by using the Doi and Edwards approach [2] (with and without taking into account the fluctuations effect), which appear less accurate. Nevertheless, this model cannot to predict the LVE of short chains ($M<4\ M_e$). This problem was partly due to the fact that we did not take into account the behaviour of the non-entangled molecules, allowing them to relax more quickly than the classical Rouse process used to describe the relaxation of a molecule in solution. But more fundamentally, this problem shows also the limitation of the tube model to describe the relaxation of short chains, recently described by Chen–Yang Liu [53]. Indeed, as shown in this work, models based on tube theory cannot predict correctly the value of the plateau modulus for samples composed of short chains. This fact is described in Figure 1, which compares the normalized plateau modulus calculated from the predictions of the very accurate model of Likhtman [10] with the plateau modulus obtained from experimental data, for polybutadiene samples.

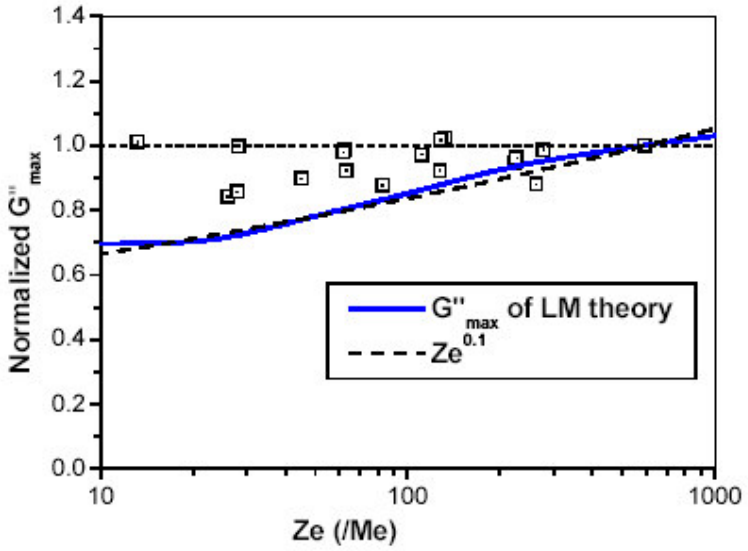

Figure 1: Normalized plateau modulus versus the number of segments per chain. Comparison between the Likhman-McLeish (LM) model with experimental data. Figure taken from [53].

Therefore, in appendix II.1, an empirical modification was proposed to slow down the relaxation of these molecules, assuming that the molecule smaller than 4 M_e relax according to a simple reptation process in stead of the double reptation mechanism.

In Figure 2, the loss moduli predicted for different monodisperse PS samples (M_w = 800, 400, 100, 40, 20 kg/mol) by using the initial TDD des Cloizeaux kernel and the double reptation (DR) concept (filled dotted line) are compared to the results obtained with the modified TDD-DR function (unfilled symbols). For samples with a molecular weight higher than 4 M_e, results are identical. But, for smaller samples, we can observe different results: with the TDD-DR model, contrary to the experimental data, a decrease of the maximum value of the peak is observed, as with the Likhtman model.

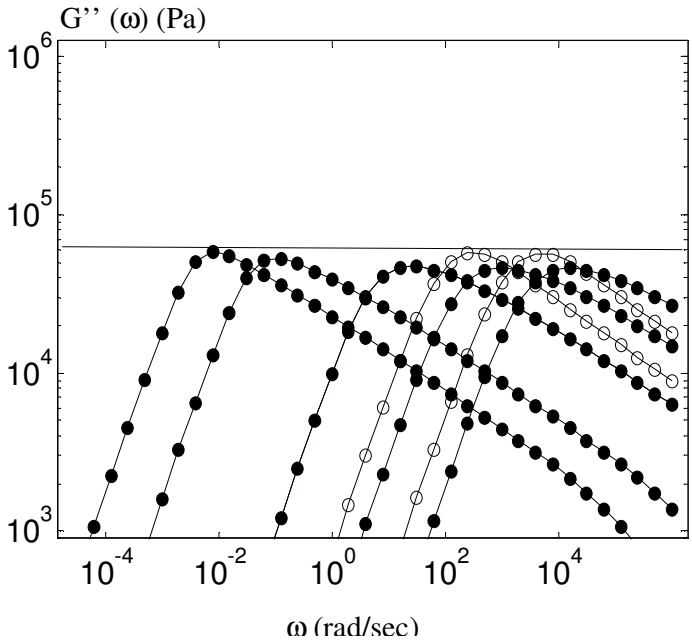

Figure 2: Theoretical loss modulus of monodisperse PS samples with different molecular weights samples (M_w = 800, 400, 100, 40, 20 kg/mol), by using the TDD-DR model (●●) and the modified TDD-DR model (oo).

But with the modified TDD-DR model, this value is identical to the one observed for long chains, the polymer fraction relaxed during the fluctuations process (for $\omega>10^4$) being less important.
Nevertheless, today, no physical explanation allows us understanding the reason of this modification. In addition, we impose it suddenly (for $M<4\ M_e$), which leads to a discontinuity in the relaxation process of the different molecules.

Another point, which is not discussed in this first appendix, is the choice of the material parameters. In this work, we have taken from literature the values of the plateau modulus and of the molecular

weight between two entanglements. They are not fit-parameters, contrary to the Rouse factor K_{Rouse}, the reptation factor K_{rept}, and the fluctuations factor, M*. Theoretically, K_{Rouse} and K_{rept} are linked. In order to respect this relation, we should take another value for M_e. We have also to remark that other set of parameters can also be convenient to predict a similar viscoelastic behaviour.
The dilution exponent, α, is generally found between 1 and 1.3 [46,47]. Here, we have decided to use an average value of 1.2. But good predictions are also obtained with other values as, for example, 1.3. Today, it appears that, to define an accurate value of this exponent, a sample with a broad molecular weight distribution must be used for calibration. (The opposite case is a monodisperse sample, which shows almost no dependence on α.)

In appendix II.2, the inverse problem of predicting the MWD of a linear polymer from its linear viscoelastic properties has been investigated. By means of a parametric method using seven parameters to build the MWD, and working with the modified TDD des Cloizeaux kernel, we have obtained very good results for a large range of polymers. We have also carried out several tests in order to understand the various factors influencing the quality of predictions. We have concluded that the inclusion of the Rouse process is important, allowing us considering the whole range of frequencies for the storage and loss moduli to calculate the MWD. So doing, we have obtained very accurate results. When approximated by two GEX functions, the real MWD can be relatively well described. Because of its ill-posedness, we cannot solve this problem with three GEX functions (i.e. 11 parameters).

Today, a question is still remaining: what about branched molecules? But the ability to predict the topology of a molecule from its LVE, on top of its length, seems unrealistic. Indeed, different architectures can lead to the same viscoelastic response. Nevertheless, it whould be interesting to test the inverse problem in the case of very well-defined architectures as, for example, a blend of star molecules, with a minimum of parameters, as with a simple GEX function (or another

function requiring only 3 parameters). The PMMA samples presented in the appendix II.5 could be used for this test.
Furthermore, if we were able to predict the LVE of the PC analysed in appendix II.6 (i.e. by taking into account the relaxation of the H or more complex molecules (see below)), it would also be interesting to test the inverse problem. Indeed, only two parameters (M_n and the branching density) are enough to describe the entire MWD for this kind of statistical polymers, which should strongly reduce the ill-posedness of this problem.
Because PC samples are industrial polymers, the ability to define which polymer we need (in term of M_n and the branching density) in order to obtain a specific rheological behaviour becomes of great interest from an industrial point of view.

These two last years, based on the direct and inverse problem presented in appendix II.1 and II.2, we have had the opportunity to compare our method with the other models proposed by several groups [54] in the frame of an international benchmark coordinated by BASF (Dr. Martin Laun). Several PS samples have been analysed by the different groups after defining the material parameters on two calibration samples. We have concluded that the predictions obtained by all the groups are more or less equivalent, and are in good agreement with the experimental data. Nevertheless, if we look at the prediction of the compliance for a polydisperse sample versus its polydispersity, large discrepancies appear between the models. In the future, it should be very interesting to do some compliance measurements, in order to know the real behaviour of these samples.

Besides the above-mentioned benchmark to compare the model, another benchmark, to test the reproducibility of the experimental results (rheological data and SEC data) has been performed. Here, we have concluded that the discrepancies between experimental relaxation moduli, which have been measured in different laboratories, are really not negligible. Sometimes, they are higher than the discrepancies observed between the different models. On the contrary,

the SEC data measured by three different laboratories were found very similar.

In appendix II.3, we have used our model to detect long chain branching (LCB) of different High Density Polyethylene (HDPE) samples, and compared it with different detection methods, such as the calculation of activation energies or the comparison between zero-shear viscosities. An important point in this work has been the observation of the thermorheological complexity for the branched PE, even at very low LCB levels. Although it was possible to construct master curves which look good, we have observed, for example by using the van Gurp-Palmen plots, thermorheological complexitity of our polymers. The analysis of the activation energies spectrum calculated from the shift factors on the storage modulus G'(ω) at each frequency (after a vertical shift) is also a good method (as proposed by Wood-Adams). It is interesting to compare this activation energies spectrum with the one obtained by considering the shift factor on tan (δ) instead of the shift factor on G'. The advantage of working with tan(δ) is to have no vertical shift. Figure 3 compares these different results for the Ziegler Natta HDPE and the Phillips PE described in appendix II.3.

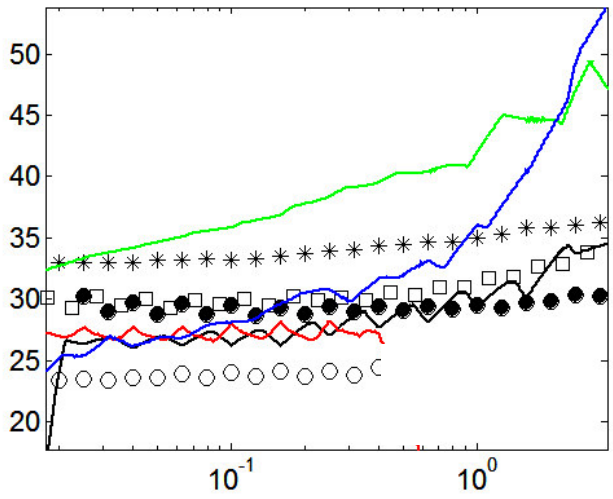

*Figure 3: Activation energies spectrum calculated from the horizontal shift factor on G'(ω) (**: pPE, ●●: zPE, : F2, oo: F1) or on tan δ (green: pPE, black: zPE, blue: F2, red: F1).*

The difference observed between both methods is not very clear for us, which suggest the validity of the tan δ-based approach. More fundamentally, the origin of the thermorheological complexity of PE is still an open question today[37].

From a rheological point of view, the analysis of the discrepancy between experimental relaxation moduli and the ones predicted by assuming linearity of a sample seems to be a good way to detect LCB. But at the moment, we cannot quantify LCB with this method. This remains one of our long-term goals. To this end, the study of commercial polymers with a well-defined structure as, for example, the PC analyzed in appendix II.6 (see below), is certainly easier.

In Appendix II.4, we have developed a single model based on tube theory, valid for a broad range of architectures. Indeed, our model, which has been validated on a large set of experimental data taken from literature, is suitable for predicting LVE of arbitrary mixtures of stars and linear molecules: monodisperse (a)symmetric star or linear polymers, bidisperse star or linear polymers, mixtures of linear and star molecules and polydisperse star or linear polymers. Because we use a time marching algorithm, which updates the unrelaxed part of the polymer at each time step, no analytical expression of the relaxation times is required a priori. Therefore, contrary to the models previously proposed in literature [3,23-25], we do not have any limitation on the polydispersity of the polymer. In addition, this allows us to include gradually the polymer fraction relaxed by reptation and to consider progressively its influence on the different fluctuations times, contrary to the models previously proposed, which consider the reptation of a molecule as a step function [23,25]. In order to identify clearly the contribution of each segment to relaxation moduli, we have also proposed a new expression for the calculation of the latter, which calculates exactly the relaxation state of each segment at a fixed time.

Furthermore, an important discussion point is the polymer fraction acting as a solvent for the relaxation of still oriented molecules. Still today, the differences between the approaches to describe this phenomenon (like constraint release, tube dilation, dynamic dilution or double reptation) are not consistent, and their limitations are not always taken into account.

In our work, we use the dynamic tube dilation picture, which is a simplified picture of the reality. Indeed, the relaxation of an observed molecule is influenced by the motions of its surrounding chains. These last ones activate the motion of the observed molecule in a direction lateral to its backbone. This phenomenon is generally called the Constraint Release (CR) mechanism [55,56], which allows local CR jumps of the segments of a chain, and which competes with the longitudinal motion of the chain along its tube axis. Therefore, to determine the viscoelastic relaxation of the polymer, a full analysis of the motion of individual entanglement segments should be required.

In order to simplify the description, the Dynamic Tube Dilation (DTD) concept has been proposed [17,55,56], that we use in appendix II.4. It assumes that relaxed portions of the chains in the system are equivalent to a solvent, considering that the segments are instantaneously mutually equilibrated through their CR motion. Therefore, the CR mechanism can be modelled by the relaxation of the molecules through only their longitudinal motion along a dilated tube, which gives a much simpler formulation of the relaxation function. Under this hypothesis, the relaxation function, $\mu(t)$ of the polymer is directly obtained from the unrelaxed fraction of its segments, $\phi(t)$ by:

$$\mu(t) = \phi(t)^{1\text{-}1.3} \qquad (1)$$

But this model fails in two different cases:

The first one occurs when a large part of the polymer relaxes in a very short time. The remaining oriented part of the polymer is then assumed to relax *immediately after* that time. However, in the real systems, the chain needs a certain time to take advantage of this CR effect. This phenomenon must be taken into account as in the Equation 29 in appendix II.4. Nevertheless, this failure does not affect the terminal relaxation region, in which the picture of DTD is generally recovered.

The second case for failure of TDT, still more fundamental, occurs when the relaxation times of the different molecules are not well separated. This has been studied by Graessley for a blend of two monodisperse linear chains composed of a small fraction of long chains in a matrix composed of very short chains [48]. According to him, if their relaxation times are not well separated enough, the short chains, even completely relaxed, do not act as a solvent for the relaxation of the long chains. Thus, in this case, the DTD picture is wrong!
Moreover, Graessley has shown that short chains behave as a solvent for the relaxation of long chains only if the relaxation (reptation) time of the long molecules ($\tau_{rept,2}$) is higher than their necessary time to relax completely by CR, $\tau_{CR}(M_2)$, which is a Rouse process:

$$\tau_{CR}(M_2) = \tau_{\mathrm{Re}\,laxation}(M_e) \cdot Z_2^{\,2} = (K_{rept} M_1^{\,3}) \cdot \left(\frac{M_2}{M_e} \right)^2 \quad (2)$$

That means that the short chains act effectively as a solvent in the relaxation of the long chains only if these long chains have had enough time to explore all the possible conformations in their "dilated tube". In other words, occupying this "dilated tube" without being capable to move freely inside it is thus not a sufficient condition to consider that the relaxation of the long chains happens in a diluted tube.

In Appendix II.4, we have extended this idea to blends of stars and linear chains or asymmetric stars and, for the first time in literature, have obtained very good predictions for asymmetric stars, without using any adjustable parameter (usually called "p^2" [25]). This is an important result.
Nevertheless, at the moment, our model does not allow considering this process as gradual. The only choice is to completely include or completely exclude the "solvent" influence. In the future, it should be interesting to improve this in order to consider intermediary states.

To still insist on the failure of the DTD picture, it is interesting to compare our conclusions with the very recent work of Watanabe [55,56], on a blend of some long linear polyisoprene chains (M_w =308 kg/mol) in different matrixes: the first one is composed of very short chains (M_w = 21 kg/mol), the second one is composed of short chains (M_w = 94 kg/mol), and the third one is a solution. In order to determine the unrelaxed part of the polymer, $\phi(t)$, without use of a reptation or fluctuations model, Watanabe measures the dielectric relaxation of the samples, which directly gives access to $\phi(t)$. Therefore, this method allows us to directly assess the validity of tube dilation. For example, Figure 4 compares the experimental relaxation function $\mu(t)$ of the PI blend composed of long chains and very short chains with the predictions based on the DTD concept (Equation 1).

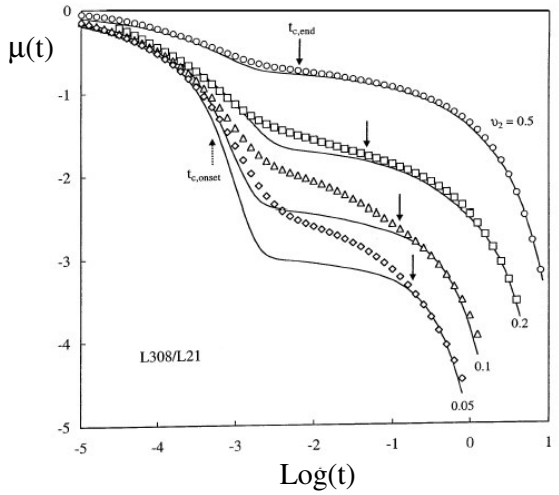

Figure 4: Comparison of the normalized viscoelastic relaxation function μ(t) (circles) with the relaxation function calculated from dielectric data (-) of a blend composed of some long chains (see their volumetric fractions in the figure) in a matrix of very short chains.

As we can observe, DTD predicts very well the first part of the relaxation of the polymer and the terminal zone, but fails in the intermediate part. First, this means that short chains act effectively as a solvent for the relaxation of the long chains in the terminal zone. Indeed, in this case, the relaxation times of short and long chains are well separated and the Graessley criterion (see Equation 19 in appendix II.4) is observed. The discrepancy in the intermediate part comes from the fact that the "solvent" coming from the relaxation of short chains appears too quickly (first case of failure of the DTD picture).

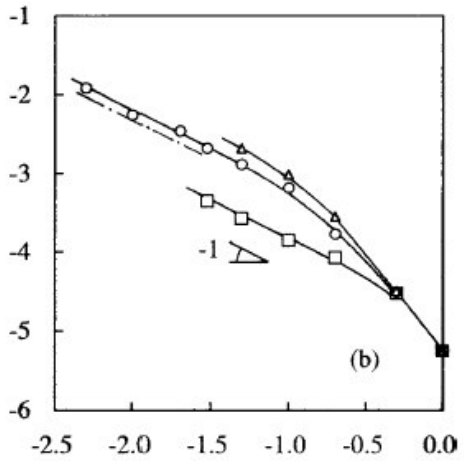

Figure 5: Experimental compliance of the long chain in different matrixes (composed of very short chains (oo), short chains ( ) or solvent (∧∧)).

In Figure 5, Watanabe compares the compliance measured for different PI blends, containing different proportions of long chains. This plot is thus a measure of the terminal viscoelastic relaxation of the polymer. As we can observed, the behaviour of the long chains in a matrix composed of very short chains is really similar to the one in a solvent, which is in harmony with the large value of the Graessley number for this case. On the contrary, long chains in a matrix of short (but not very short) chains (M_w = 94 kg/mol), do not behave like a solvent, and the DTD model fails, as expected by analysing the Graessley criterion, which is not respected in this case.

In conclusion, these very recent data confirm again the limitation of the DTD picture, in agreement with the conclusion of appendix II.4.

Appendix II.5 is a direct application of our model developed in appendix II.4: for the first time, we are able to analyze the relaxation of polydisperse stars. Results are very encouraging. The success of our

model in describing the relaxation of an already broad range of polymer structures gives some hope for understanding the dynamics of more complex systems. Indeed, its structure allows us to easily extend it to H or comb polymers and then, to proceed to polymers always closer to the industrial polymers. One of our long-term goal is, for example, the prediction of the LVE of sparsely branched polycarbonate analysed in appendix II.6.

In Appendix II.6, in order to detect LCB in Polycarbonate samples, we have compared the results of solution characterization realized by A. Kaivez with their characterization based on the analysis of the relaxation moduli G' and G".
In comparison to the results of Appendix II.3, PC samples present the important advantage that we can calculate their statistical structure by using an approach based on the Monte Carlo algorithm. This allows us to verify our predictions about the presence of LCB.
But, in addition to that, the knowledge of their complete structure represents a very good starting point to test our model developed in appendix II.4 on industrial polymers. Indeed, in a very near future, we will compare predictions and experimental data, taking into account all the asymmetric star molecules in the polymer, in addition to the linear ones. Then, the discrepancy observed between experiments and predictions should allow us to see the influence of the more complex structures. Moreover, once our model is extended to H and comb molecules, we can hope to arrive at a quantitative prediction for this kind of polymers.

To this aim, another important point will be the analysis of how to represent the total sample by a reasonable number of molecules, i.e. if it is possible to define some "average" molecules, representative of the entire sample. In this case, a method based on the graph theory could be very helpful.

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