RELATIONSHIP BETWEEN LINEAR VISCOELASTIC PROPERTIES AND MOLECULAR STRUCTURE FOR LINEAR AND BRANCHED POLYMERS

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département INMA.

FOREWORD

This document is divided into two parts. The first one introduces the subject and outlines our main results, which are described in details in the second part. Next, it introduces the physical properties and concepts about tube theory on which our work is based. Written in French, this chapter doesn't describe our own results, but should allow a person who is not familiar in the field to get the necessary background to understand the second part. Then, in the last chapter of this first part, conclusions and perspectives are presented.
The second part is constituted of seven distinct appendixes. Each of the six first ones represents a paper already published or being submitted for publication, summarized below. The seventh one presents the algorithm of the model described in appendix II.4.

Paper 1:

Evaluation of reptation models for predicting the linear viscoelastic properties of entangled linear polymers.

E. van Ruymbeke, R. Keunings, V. Stéphenne, A. Hagenaars, C. Bailly.
Published in *Macromolecules*, 35(7), 2689, (2002).

Paper 2:

Determination of the molecular weight distribution of entangled linear polymers from linear viscoelasticity data.

E. van Ruymbeke, R. Keunings, C. Bailly.
Published in J. Non-Newtonian Fluid Mech., 105, 153-175 (2002)

Paper 3:

A sensitive method to detect very low levels of long chain branching in high-density polyethylene, from molar mass distribution and linear viscoelastic response.

E. van Ruymbeke, V. Stéphenne, D. Daoust, P.Godard, R. Keunings, C. Bailly.
Being submitted for publication in *Journal of Rheology*.

Paper 4:

Prediction of linear viscoelastic properties for polydisperse mixtures of entangled star and linear polymers: Modified tube-based model and comparison with experimental results.

E. van Ruymbeke, R. Keunings, C. Bailly.
Accepted in J. Non-Newtonian Fluid Mech., 2005.

Paper 5:

Linear rheology of linear and star-shaped poly-(methyl methacrylate).

J.F. Vega, L. Xue and E. van Ruymbeke, R. Keunings, C. Bailly.
Being submitted for publication in *Macromolecules*.

Paper 6:

Characterization of sparcely long chain branched polycarbonate by a combination of solution, rheology and simulation techniques.

E. van Ruymbeke, A. Kaivez, A. Hagenaars, P. Godard, R. Keunings, C. Bailly.
Being submitted for publication.

CONTENT

PART I

PART II

APPENDIX II.1

EVALUATION OF REPTATION MODELS FOR PREDICTING THE LINEAR VISCOELASTIC PROPERTIES OF ENTANGLED LINEAR POLYMERS

APPENDIX II.2

DETERMINATION OF THE MOLECULAR WEIGHT DISTRIBUTION OF ENTANGLED LINEAR POLYMERS FROM LINEAR VISCOELASTIC DATA.

APPENDIX II.3

A SENSITIVE METHOD TO DETECT VERY LOW LEVELS OF LONG CHAIN BRANCHING IN HIGH DENSITY POLYETHYLENE FROM MOLAR MASS DISTRIBUTION AND LINEAR VISCOELASTIC RESPONSE

APPENDIX II.4

PREDICTION OF LINEAR VISCOELASTIC PROPERTIES FOR POLYDISPERSE MIXTURES OF ENTANGLED STAR AND LINEAR POLYMERS: MODIFIED TUBE-BASED MODEL AND COMPARISON WITH EXPERIMENTAL RESULTS

APPENDIX II.5

LINEAR RHEOLOGY OF POLYDISPERSE LINEAR AND STAR-SHAPED POLY-(METHYL METHACRYLATE)

APPENDIX II.6

CHARACTERIZATION OF SPARSELY LONG CHAIN BRANCHED POLYCARBONATE BY A COMBINATION OF SOLUTION, RHEOLOGY AND SIMULATION TECHNIQUES

APPENDIX II.7

PREDICTION OF LINEAR VISCOELASTICITY FOR MIXTURES OF LINEAR AND STAR MOLECULES: DESCRIPTION OF THE ALGORITHM.

PART I

CHAPTER I.1.

OVERVIEW

1.1. INTRODUCTION

The understanding of the relationship between rheological properties of polymers and their molecular structure is the subject of a longstanding interest. During the past two decades, it has considerably improved, particularly with the development of molecular-dynamics theories [1,2]. Beyond the academic interest of models relating molecular dynamics to the macroscopic viscoelastic behaviour, a fine description of the structure/viscoelasticity relationship is of the greatest interest for the polymer industry, because processing as well as the final properties of polymers are directly governed by their rheological behaviour.

To this end, "tube" models, "slip-link" models and, very recently, atomistic simulations have received tremendous attention [3-6]. In dilute solutions, the chains do not interact. The polymeric contribution to the stress is then obtained by simple addition of their individual contribution [7]. In concentrated solutions and melts on the other hand the chains overlap extensively. If they are long enough, their behaviour will be dominated by entanglement interactions, on which these models are based [1,2].

An important step for understanding of structure/viscoelasticity relationship of a polymer is the study of its linear viscoelasticity (LVE). The knowledge of its behaviour in a linear regime can indeed help us to understand its behaviour in the non-linear regime. Moreover, empirical rules like the Cox-Merz law [8], allow us to link the polymer response directly to these two regimes.

For linear polymers major progress has been realized to the point that quite accurate quantitative predictions of LVE can now be made [9-12]. The theory behind these predictions is mostly based on the reptation concept, introduced by de Gennes [1] and Doi and Edwards [2]. According to this theory, an analogy is made between the network of entanglements and a tube in which the molecules are confined. This tube prevents the lateral motions of a chain and forces it to move along the curvilinear tube axis. The reptation consists in this diffusion process, allowing the chain to leave this oriented tube.

Inverse predictions of molecular weight distributions of linear polymers from the knowledge of their rheological response are also of considerable interest [13-16]. First, this method can be used to characterize a linear polymer, without putting it in solution. Secondly, it allows us to determine the a-priori MWD of a polymer in order to obtain a specific rheological behaviour. Because this problem is ill-posed, several solutions, mostly based on a parametric representation of the MWD have been proposed to solve it [13,15].

The situation for branched polymers is much more complicated for at least two reasons. First, because of the incredible variety of architectures that can be, and actually are, made in laboratories or by the industry. Many more parameters are needed to describe complex branched architectures than for linear ones, which can adequately be reduced to a few moments of a molecular weight distribution or a limited number of fractions. It has further been recognized quite early that branched polymers are characterized by very broad distributions of relaxation times, which are very dependent on details of the architecture [17]. In this case, branch points prevent reptation. Instead, stress in star polymers relaxes by arm fluctuations: the free end of an arm can retract along its own tube and then explore a new path by extending back in another direction [3].

To address the issue of branched architectures from a molecular theory standpoint, it is quite essential to study model systems with a limited and controlled level of complexity. This explains why many recent studies have been devoted to the prediction of LVE for ideal model molecules, mainly monodisperse stars [3,18], H-shaped or POM-POM molecules [19,20] and combs [21,22]. Some studies on simple mixtures of star architectures [23] or mixtures of stars with linear chains [24] or asymmetric stars [25] have also been published. For the analysis of more complex structures two main molecular approaches have been proposed. The first involves the hierarchical description of an explicitly described complex molecule, leading to a hierarchy of relaxation processes [23-25]. Another approach is to reduce empirically the complex architecture to a mixture of simple model molecules (for instance POM-POM molecules [19,20]), which will of course also implicitly reflect the hierarchy of the real architecture.

In addition to reptation and fluctuations processes, the motions (relaxation) of the chains around an observed molecule (linear or branched), will lead to the lost of entanglements, which maintained the molecule in its orientated state. This will allow the molecule to move laterally out of its tube. This mechanism is called “constraint release”. To describe it several models have been suggested including “double reptation”[26,27], “constraint release Rouse motion” [4,24] and “dynamic tube dilation”[17,28]. Moreover, this relaxation process has an influence on the specific reptation and fluctuation times of the chains [3,29]: the polymer fraction already relaxed will act as a solvent during the relaxation of the polymer fraction, which is still oriented.

The objective of this work strives towards the long-term goal of a quantitative theory for the prediction of the linear rheological response of a statistical polymer. In particular, we want to understand, to test and to improve the different approaches based on tube theory proposed in the literature for simple model molecules. The key idea of this work is to propose a single model able to predict the LVE of a large range of polymers with different structures, linear or branched, monodisperse or polydisperse. Indeed up to now models used to predict the LVE of polydisperse linear chains do not allow analyzing branched molecules, and models used for monodisperse or bidisperse star molecules cannot be extended to a polydisperse star polymer nor to a polydisperse linear polymer. In addition to that, theory fails to predict the behaviour of asymmetric stars [25]. It prevents the extension of the models to more complex structures (thus, closer to industrial polymers).

The ability to predict quantitatively the LVE of linear polymer can also be used to characterize long chain branching (LCB) in a polymer melt. Indeed, rheological measurements are known to be very sensitive to LCB. Hence analyzing the discrepancy between experimental relaxation moduli (G'(ω) and G"(ω)) and their prediction, assuming the linearity of the polymer, can give us important information about its structure. Therefore, a second objective of this work is to compare this new characterization technique, based on our modeling, with the more classical techniques commonly used to detect LCB (i.e. solution characterization or other rheology-based methods) [30-35].

1.2. MAIN RESULTS

Our main results are described in the second part of this document, and are summarized below:

***Appendix II.1*:**

Evaluation of reptation models for predicting the linear viscoelastic properties of entangled linear polymers.

E. van Ruymbeke, R. Keunings, V. Stéphenne, A. Hagenaars, C. Bailly, *Macromolecules*, 35(7), 2689, (2002).

This work has been presented in several meetings:

1) *3rd Int. Conf. On the Dynamics of Polymeric Liquids, Capri, Italy (May 2002)*

2) *Cambridge, England (December 2002).*

3) *Symp. "Polymers in the 3d Millennium", Univ. Montpellier II Sciences et Techniques du Languedoc, France (September 2001)*

4) *Conf. Of the European Polymer Federation, Eindhoven, The Netherlands (July 2001)*

5) *2nd Int. Workshop on Inverse Problems and Emerging Techniques in Materials Characterization, Badenweiler, Germany (May 2001)*

6) *AIChE 2000 Annual Meeting, Los Angeles, USA (November 2000)*

7) *1st Int. Workshop on Inverse Problems and Emerging Techniques in Materials Characterization, Lake Vyrnwy, Mid Wales (April 2000)*

First, we study the different reptation models proposed in the literature and do a systematic comparison between the predicted and experimental viscoelastic behaviour of various combinations of almost monodisperse, bidisperse and polydisperse polystyrene (PS), high density polyethylene (PE) and polycarbonate (PC) samples, starting from their molecular weight distribution. In each case, the constraint release effect is added to models by using an approach based on the double reptation idea. The Rouse process, ordinarily used to describe the relaxation of a dilute solution, is also added. We propose a new expression to describe it, allowing to predict very well the relaxation moduli, G' and G", at high frequencies.

Figure 1 compares experimental data with predictions obtained for a bidisperse PS (50% PS 190000 g/mol and 50% PS 920000 g/mol), by using either the original Doi and Edwards model, or their model including the influence of tube length fluctuations on the relaxation time, or the Time Dependent Diffusion des Cloizeaux model. They are representative of the other results that we have obtained.

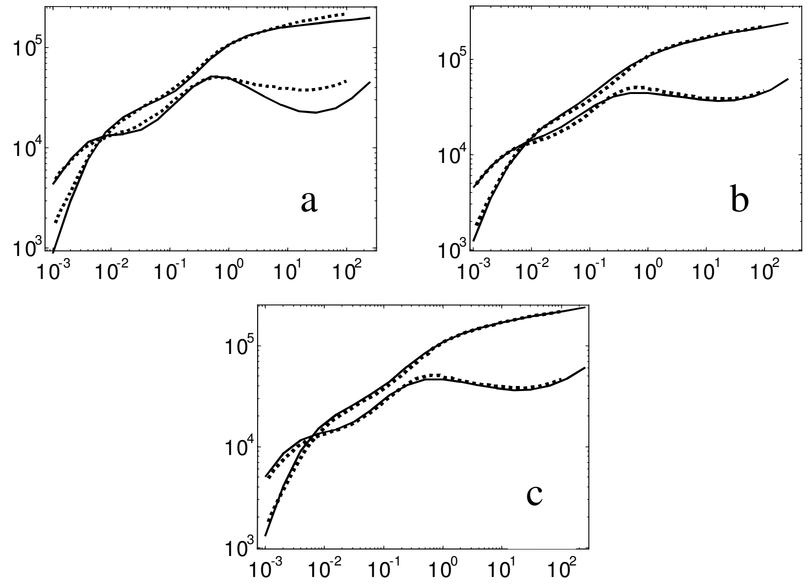

Figure 1: Comparison between experimental (…) and theoretical (—) G'(ω) and G"(ω) of a bidisperse PS (50% PS 190000 g/mol and 50% PS 920000 g/mol), by using a) the Doi and Edwards model, b) the Doi and Edwards model including fluctuations, c) the TDD des Cloizeaux model.

The initial model of Doi and Edwards is not fit to take into account the fluctuation effect, which explains why its predictions are not accurate in the intermediate part (see Figure 1.a). Generally the model of Doi and Edwards including fluctuations, and the Time Dependent

Diffusion des Cloizeaux model predict effectively the linear viscoelasticity (LVE) of linear polymer. Nevertheless, the model of des Cloizeaux gives slightly better results than the model of Doi and Edwards. This relaxation function is based on the fact that the diffusion of a chain along its curvilinear tube axis is represented by a non-constant diffusion coefficient in order to include the fluctuation effect in the relaxation of the polymer melt. Indeed this diffusion coefficient, used to calculate the reptation time of a chain, starts from an infinite value and decreases through time down to its usual constant value proposed by the model of Doi and Edward. So, imposing that in a first stage, molecules move quicker than in the next, des Cloizeaux establishes the same effect than the one of the fluctuations.

Nevertheless, as presented in Figure 2.a, this model fails for LVE prediction of polymer composed of short chains (slightly longer than the critical molecular weight to be well-entangled). Therefore, we propose a modification, which allow us to obtain quantitative results for all the samples analyzed, including this last kind (see Figure 2.b).

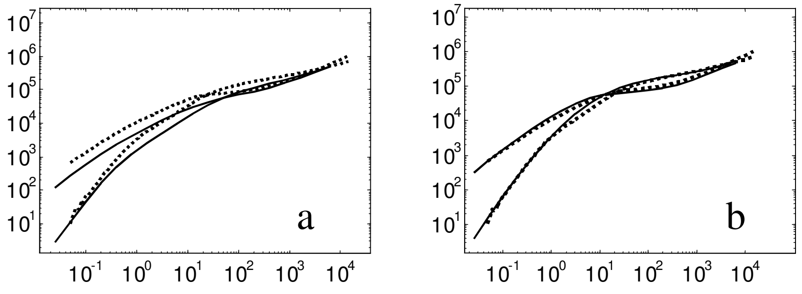

Figure 2: Comparison between experimental (…) and theoretical (—) G'(ω) and G"(ω) of a bidisperse PS composed of short chains (80% PS 68000 g/mol and 20% PS 170000 g/mol), by using a) the initial TDD des Cloizeaux model, b) the modified TDD des Cloizeaux model.

Appendix II.2:

Determination of the molecular weight distribution of entangled linear polymers from linear viscoelasticity data.

E. van Ruymbeke, R. Keunings, C. Bailly. *J. Non-Newtonian Fluid Mech.*, 105, 153-175 (2002).

This work has been presented in several meetings (see meetings 2 to 7 in Appendix II.1)

Here, we use the TDD des Cloizeaux model to address the inverse problem of predicting MWD from relaxation moduli, which can be an alternative or complementary method to the SEC (no solution required). A parametric approach has been implemented to deal with the ill-posed problem. To this end, we have used the generalized exponential (GEX) function, which is described by only three parameters, *a*, *b* and M_0:

$$w_{GEX}(M) = C.\left[\frac{M}{M_0}\right]^{a+1} \exp\left(-\left[\frac{M}{M_0}\right]^{b}\right) \tag{1}$$

This function is a generalization of a large number of physically relevant molecular weight distributions including those of Flory, Schultz, Tung and Weibull. It is therefore an ideal parametric description of monomodal distributions, with more generality than Gaussian or log-normal distributions.

The three parameters are determined by a last square minimization procedure (based on the Nelder Mead simplex method) on the relative error between experimental moduli $\{G'_{exp,i}, G''_{exp,i}\}$ measured at the frequency set $\{\omega_i\}$ for i = 1, 2, …, n_{exp}, and theoretical moduli $\{G'_{theor,i}, G''_{theor.,,i}\}$ computed at the same frequencies with the modified TDD des Cloizeaux model for an assumed GEX distribution. We test through iterations the convergence of the error as well as the convergence of the average molecular weights of different polymers.

We test also the influence of the frequency range considered for the predictions. We extend the method to a double GEX function (described by 7 parameters), which is useful to predict the MWD of a bidisperse sample but also to obtain a higher accuracy for prediction of the MWD in case of polydisperse polymers. Then, we show that the inclusion of the Rouse relaxation at high frequencies is indispensable to correctly predict MWD of short chains. Results obtained for a wide range of polymers with various MWD shapes are in quantitative agreement with SEC data (see, for example Figure 3.a). In particular, as shown in Figure 3.b, the proposed methodology is adequate to resolve small amounts of short chains in bimodal blends containing large amounts of long chains.

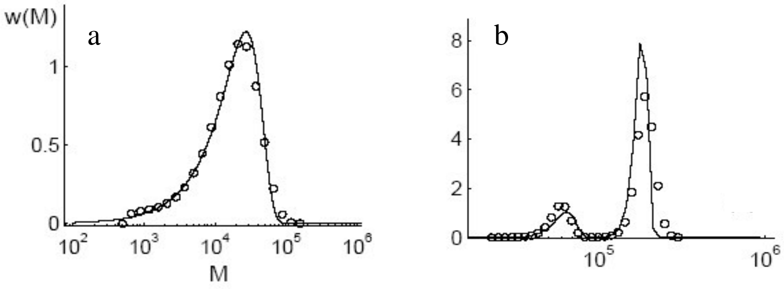

Figure 3: Comparisons between SEC data (°°°) and predictions (—), obtained for a) a polydisperse polycarbonate sample, b) a bidisperse PS (20% 54000 g/mol and 80% 190000 g/mol).

Appendix II.3:

A sensitive method to detect very low levels of long chain branching in high density polyethylene, from molar mass distribution and linear viscoelastic response.

E. van Ruymbeke, V. Stéphenne, D. Daoust, P.Godard, R. Keunings, C. Bailly; submitted for publication in *Journal of Rheology*.

This work has been realized in collaboration with Vincent Stephenne (POLY, UCL), who has fractionated and characterized the samples analyzed. It has been presented in two meetings:

1) *226th ACS National Meeting, Symposium "Branching in Polyolefins", New-York, USA (September 2003)*

2) *1rst Ann. European Rheology Conf. (AERC 2003), Guimarães, Portugal (September 2003)*

In this work, we use the modified des Cloizeaux model to detect very low levels of long chain branching (LCB) in sparsely branched high-density polyethylene. We analyze samples with broad molar mass distribution such as Ziegler-Natta (zPE resin), Chromium and metallocene-catalyzed high-density polyethylenes, as well as fractions obtained by Successive Solution Fractionation on the Ziegler-Natta sample [36]. The procedure is based on the comparison between experimental dynamic moduli and predicted values determined by assuming that the polymers are linear. Thus, discrepancies between experiments and rheology inform us about the presence of LCB (see Figure 4).

Because this kind of branched polymers is thermorheologically complex, no single horizontal shift factor can be found. Therefore, we apply the method proposed by Wood-Adams in order determine the activation energy spectra [37]. Then, we compare the proposed LCB characterization method with more classical rheology-based methods and with C-nuclear Magnetic Resonance (NMR). Its sensitivity is comparable to the one based on the activation energy spectrum analysis and more sensitive than ^{13}C-NMR method. Contrary to the zero-shear viscosity approach, our method is easily applicable to HDPE characterized by very long relaxation times. On the other hand, our method is not applicable to polymers with LCB level so low that rheological behavior is not significantly affected in the experimental frequency window. In such cases, the interest of MM fractionation has been emphasized. Presence of LCB on the longest molecules has been revealed in this manner for the Ziegler catalyzed HDPE sample.

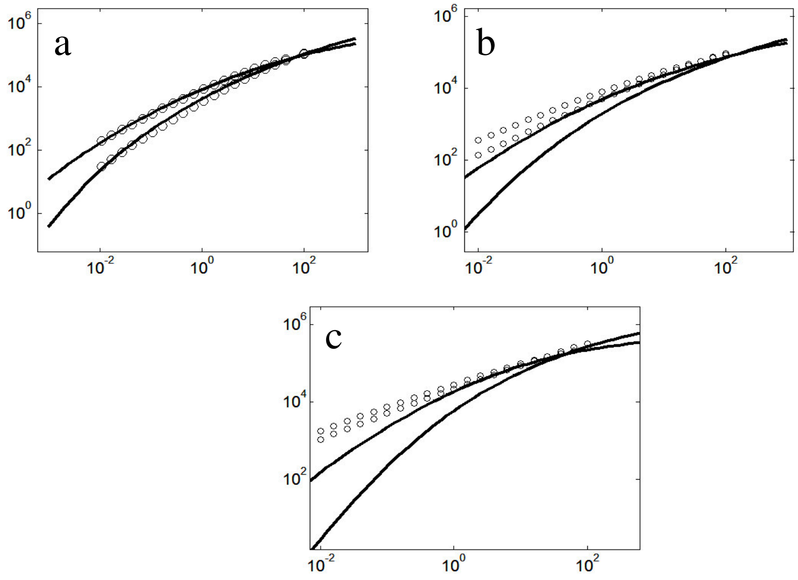

Figure 4: Comparison between experimental (…) and theoretical (—) G'(ω) and G"(ω) of a) a Ziegler-Natta, b) a Chromium, c) a metallocene HDPE. Predictions assume that these polymers are linear. The more important the discrepancy between theory and experiments, the more important is the LCB level of the polymer analyzed.

***Appendix II.4*:**

Prediction of linear viscoelastic properties for polydisperse mixtures of entangled star and linear polymers: Modified tube-based model and comparison with experimental results.

E. van Ruymbeke, R. Keunings, C. Bailly. Accepted in *J. Non-Newtonian Fluid Mech.,* 2005.

This work has been presented in several meetings:

1) *2nd Annual European Rheology Conference, Grenoble, France (April 2005)*

2) *The Society of Rheology: 76th Annual Meeting, Lubbock, USA (February 2005)*

3) *14th International Congress on Rheology, Symposium "Microstructural Modeling", Seoul, Korea (August 2004)*

4) *Int. Workshop on Industrial Rheology, Chester, UK (April 2004)*

5) *ICR in Polymer Science and Technology, Departement of Physics and Astronomy, Leeds, England (January 2004)*

6) *1rst Ann. European Rheology Conf. (AERC 2003), Guimarães, Portugal (September 2003)*

7) *Proc. 6th Nat. Congress on Theoretical and Apllied Mechanics, Gand, Belgium, (May 2003)*

In order to be able to predict the linear viscoelasticity of more complex molecules, like arbitrary mixtures of (asymmetric) star and linear entangled molecules, we develop and test a new model, which contains the key ingredients of tube models: reptation, fluctuations, constraint release and tube dilation. Reptation and fluctuations are treated in a classical way. However, we impose no artificial time scale separation between fluctuations and reptation processes but rather treat both as simultaneous and progressive. Early fluctuations are treated in a new way, simple but effective, based on a potential versus thermal energy level criterion. This treatment has the advantage to be applicable to complex mixtures of molecules and gives excellent results. Because the systems modelled can be arbitrary mixtures, there can be no analytical solution and a time-marching algorithm must be used. At each time step, the key parameters to be calculated are the reptation and fluctuations times of each segment. To this end, the interrelations between fluctuations and reptation processes must be taken into account very carefully through the inclusion or exclusion of the constraint release solvent in the relaxation process under consideration. We come to the conclusion that a generalization of the concept of “Graessley number”, i.e. the ratio of a characteristic constraint release time over a characteristic relaxation time, can be used as a criterion for the decision to include or exclude the solvent and thus to consider the skinny or the dilated tube for the relaxation process. The model is tested on a wide range of literature data pertaining to PBD, PI and PS model systems, leading to excellent quality predictions, provided that the constraint release solvent is correctly treated. In particular we do not need to impose artificial simplifications (reptation as time-step process) or ad hoc parameter modifications for asymmetric stars to get equivalent predictions to those already published. Moreover, with a slight exception concerning the dilution exponent for PI, the same material parameter values can be used for all the corresponding literature data, emphasizing the consistent nature of the proposed model. Figure 5 compares experiments and theory of a blend of linear (M_w = 105000 g/mol) and star molecules ($M_{w,arm}$ = 42000 g/mol), in different proportions, while Figure 6 presents the results obtained for asymmetric stars (composed of two long arms and one short arm), without any additional adjustable parameter.

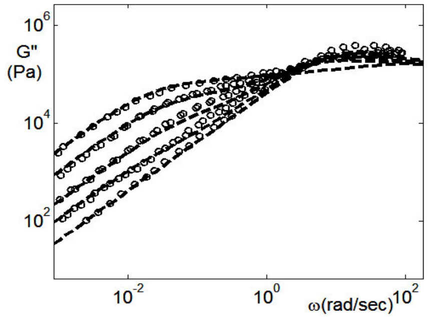

Figure 5: Comparison between experimental (◦◦◦) and theoretical (—) G”(ω) for a mixture of linear molecules (M_w=105000 g/mol) and monodisperse star polybutadiene ($M_{w,arm}$=42000 g/mol), in different proportions (from left to right: 0%, 20%, 50%, 75%, 100% of stars).

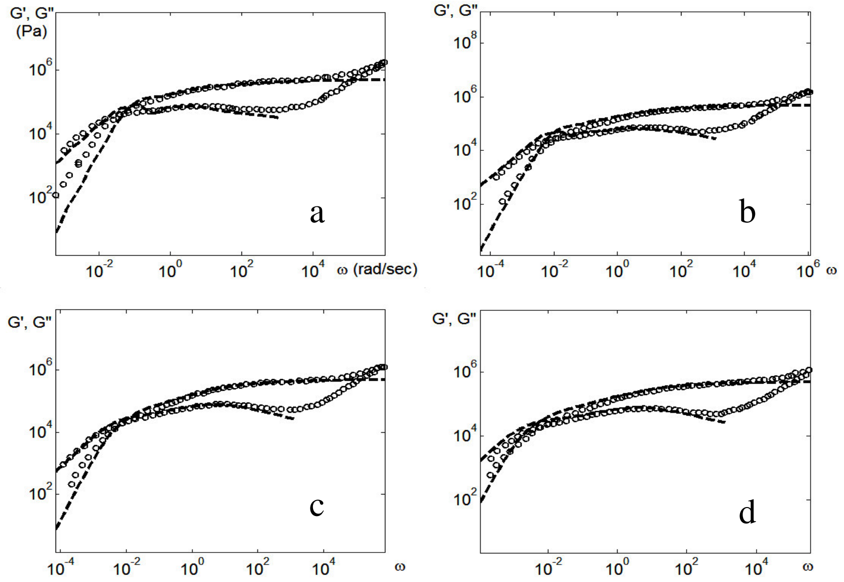

Figure 6: Comparison between predictions (---) and experimental data (◦◦◦) of asymmetric star polybutadiène. The backbone length is 107000 g/mol, and the short arm length is a) 11000 g/mol, b) 17000 g/mol, c) 39000 g/mol, d) 38000 g/mol.

Appendix II.5:

Linear rheology of linear and star-shaped poly-(methyl methacrylate).

J.F. Vega, L. Xue and E. van Ruymbeke, R. Keunings, C. Bailly; being submitted for publication in *Macromolecules*.

Rheological experiments and analysis of viscosity and compliance have been realized by Prof. J.F. Vega (Eindhoven). The synthesis and characterization of the samples have been carried out by L. Xue (Eindhoven).

The linear dynamic viscoelastic properties of linear and 6-arm star poly-(methyl methacrylate) (PMMA) obtained by atom transfer radical polymerization [38] and characterized by a narrow – but polydisperse - molecular weight distribution (Ip ≈1.25) is analyzed. The complete linear viscoelastic response is obtained in a broad range of temperatures. Contrary to the polyethylene samples analyzed in Appendix II.3, no signs of thermorheological complexity are observed for star samples, similarly to other long chain branched polymers with big side groups as polystyrene and polyisobutene. Newtonian viscosity and steady-state compliance of the star samples follow the expected behaviour of star branched polymers. Only slightly higher values of the steady-state compliance compared to those expected for monodisperse samples are obtained. The entanglement state defined by means of the plateau modulus G_N^0 is similar to that shown by samples of similar tacticity. The characteristic Rouse time of a segment between entanglements, τ_e, is determined by means of the universal curve $\eta_0 G_N^0/\tau_e$ *versus* N_e for star molecules.

Then, the linear viscoelastic response of the samples is predicted using two different theoretical approaches based on reptation, fluctuations and tube concepts, and taking into account the effect of the molecular weight distribution: the Doi and Edwards model including fluctuations (see Appendix II.1) and the model developed in Appendix II.4. In general, a very good agreement between models and experimental results is observed by using a common set of parameters for both linear and star samples: the entanglement plateau modulus, G_N^0, and the Rouse relaxation time of a segment, τ_e. In particular, the Figure 7 shows the predictions for the polydisperse star PMMA. This kind of data has never been predicted before in literature.

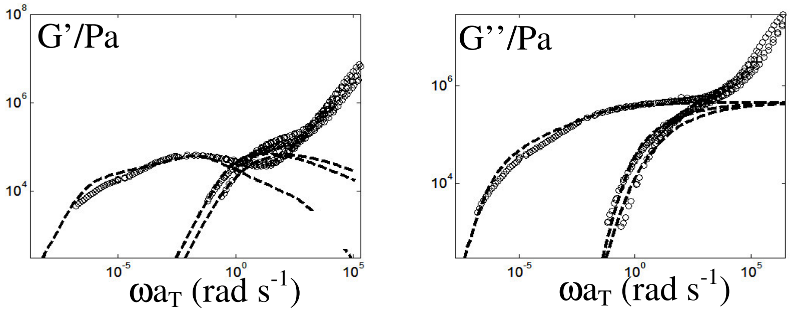

Figure 7: Comparisons between experimental (◦◦◦) and theoretical (--) G' (a) and G'' (b) of star branched PMMA samples at a reference temperature 190ºC, with (from right to left:) M_w = 130500, 210600 and 2500000 g/mol.

The accuracy of the predictions also confirms the precision of the techniques used to synthesize and characterize the PMMA samples [38]. Nevertheless, for one of the star samples, disagreement between rheological predictions and experiments, together with the observation of a shoulder in its MWD, seems to indicate the presence of some star-star coupling molecules.

Appendix II.6:

Comparison between solution and rheological characterization of long chain branched polycarbonate.

E. van Ruymbeke, A. Kaivez, A. Hagenaars, P. Godard, R. Keunings, C. Bailly; being submitted for publication.

The samples have been synthesized and fractionated by A. Hagenaars (POLY, Université catholique de Louvain). The solution characterization has been realized by A. Kaivez (POLY, Université catholique de Louvain).

In this work, we compare solution (SEC- viscometry coupling) and rheological characterization method to detect long chains branching in two slightly branched PC synthesized by melt transesterification and in fractions of the same [39]. In solution, branching were characterized by analyzing the local intrinsic viscosity of the samples in function of their molar masses, as well as their local branching factor g' ($g' = ([\eta]_{br}/[\eta]_{lin})_M$ where $[\eta]_{br}$ and $[\eta]_{lin}$ are the intrinsic viscosities of respectively branched and linear polymers of the same molar mass). The curve of g' obtained for the more branched PC (ρ = 2.955 br./1000 monomers) is shown in Figure 8. In the case of the total sample as well as for its fractions, the effect of long chain branching is clear for molecules longer than 40000 g/mol. The solution analysis of the very slightly branched PC (ρ = 1.07 br./1000 monomers) does not allow us to conclude anything, even for its highest fraction.

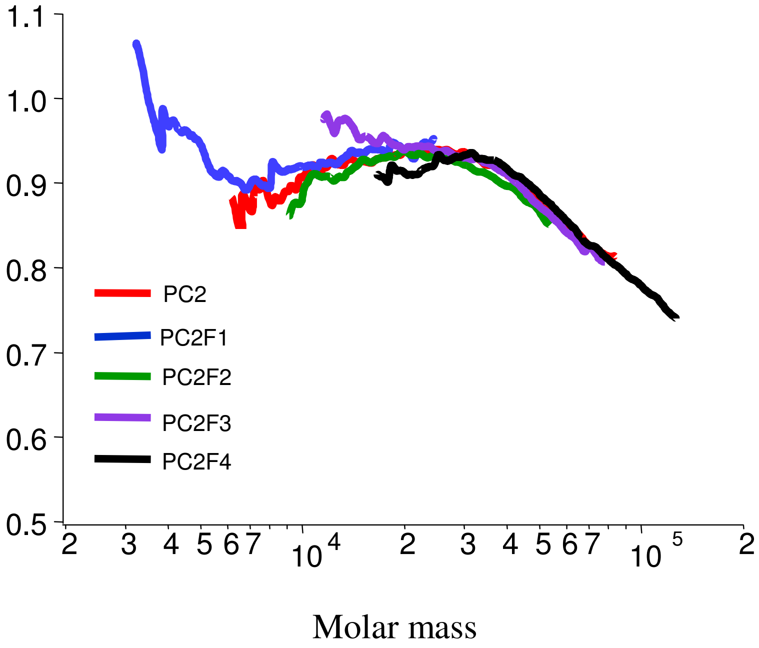

Figure 8: Local branching factor g' of a slightly branched PC with ρ = 2.955 br./1000 monomers (PC2), and of its fractions (PC2F1, PC2F2, PC2F3, PC2F4).

Next, after its calibration on a linear PC, our model (described in Appendix II.4) is used to predict the linear viscoelasticity of these samples from their MWD, assuming that these are linear. From discrepancies between predictions and experimental data, we derive some important indications about the presence and the level of long chain branching in the samples studied (with a technique similar to the one proposed in Appendix II.3). Figure 9 compare predictions and experiments for the more branched PC and for its highest fraction. In both these cases, as well as for the other fractions, LCB are detected.

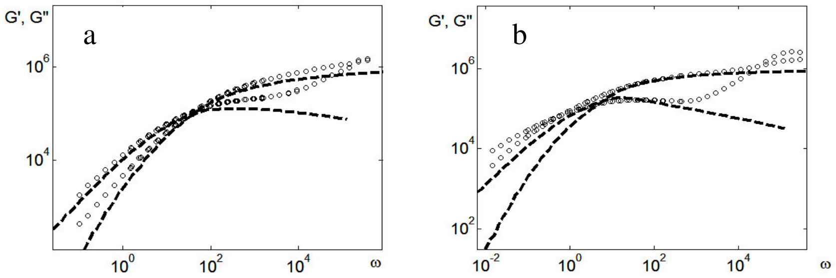

Figure 9: Comparisons between experimental (◦◦◦) and theoretical (--) G' and G" of a) the slightly branched PC with ρ *= 2.955 br./1000 monomers, and of its higher fraction.*

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With the very slightly branched PC sample (1.07 br./1000 monomers), we cannot detect any LCB on the total sample or on its lower fractions. Nevertheless, the comparison of the relaxation moduli for its higher fraction shows distinctly a discrepancy between experiments and theory, which shows that it is branched.

Then, to validate our characterization results, we have elaborated a program based on the Monte Carlo algorithm, appropriate to re-construct statistically the unfractionated PC from their average molar mass in number, M_n, and of their branching density, ρ. This method presents the advantage of allowing us to know exactly the shape of each molecule constructed, from which several studies have been done, like the visualization of the proportion, the shape and the localization of the branched molecules. Comparisons with statistical results have allowed us to discuss about the advantages of each characterization method.