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"Mechanical Pretreatment of Polymer Melts: Critical Aspects and New Rheological Investigations on a Linear and a Long-Chain Branched Polypropylene" by Helmut Münstedt, J.O.R., 65.5(2021): 871-885, DOI: 10.1122/8.0000287

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- There is no good reason to doubt and attempt to disqualify the results on the shear-induced melt instability of linear polymers (designated "disentanglement" in our work, "shear-refinement" by Munstedt). Münstedt's misquotes were corrected and their implications refuted.
- Münstedt used the classical topological description of long chain branched (LCB) polymers to support his opinion that linear chain polymers cannot qualify to successfully induce shear-refinement effects. We argued that although LCBs and linear chains are architecturally different, the true cause for shear-refinement must be found elsewhere, and we pointed to the dynamic free volume as one of the causes of the melt instability triggering a reduction of viscosity. LCB polymers have inherently more dynamic free volume than the linear polymers, a positive attribute for shear-refinement, but both architectures can support a substantial enhancement of dynamic free volume by melt Rheo-Fluidizing manipulation, not just the LCB type. The dynamic free volume is quantified by the Grain-Field Statistics model of the interactions but not by the molecular dynamic models.
- The reluctance to accept the "melt instability" experimental results by Münstedt was perhaps motivated by the lack of molecular dynamic models' arguments to comprehend them.
- The discovery of the instability of the entanglement network triggers the necessity to understand entanglements differently.
- We briefly introduce the general principles underlying the *Grain-Field Statistical model of interactive coupling of dissipative systems* that we believe could become the basis for a new paradigm in polymer physics beyond the current limitations of the molecular dynamic models (Rouse and reptation) that have dominated our academic interpretation of the deformation of macromolecular chains but fail to construe new experimental evidence (e.g. "Sustained-Orientation", the T_{LL} transition).

I. INTRODUCTION

The purpose of Münstedt's paper is clearly stated in his title and in the abstract: taking polypropylene (linear and long chain branched) as the polymer of investigation, and reporting other similar results taken from the literature using different polymers, Münstedt concluded :"*A widerange of linear and nonlinear rheological properties was studied, and it became obvious that long-chain branching is a strong structural precondition for the pronounced pre-treatment effect occurring in processing*". In other words, Münstedt affirms that based on his review of the literature and his own work on polypropylene, there is no substantial effect of a mechanical pre-treatment if one uses a linear polymer, only long chain branched polymers (LCB) will work. This conclusion is contradicting our own experience and publications on this subject [4-40], summarized in Ref. [2], that Münstedt quoted and discussed in his paper.

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"*This* (pre-treatment) *effect is sometimes called "shear modification" or "refining"*", says Münstedt. Other terms have been used more recently: "disentanglement" was used by this author in early experimental work on this subject which started in 1997-1999 [4-13], and continued on for the last 20 years [14-40]. As our critical progress in understanding the origin of this pre-treatment effect on the rheological properties of melts became quantifiable by our model of interactions, the "disentanglement" effect was re-qualified as "the melt shear-induced instability" and we decided to write an introductory book to report the experimental evidence on the instability of entangled melts[2]. The book reviews several aspects of the rheology of polymer melts, showing some of the problems the current theoretical models face in particular with respect to explaining the instability of the melts under non-linear shear stresses. These are the experiments of the book quoted by Münstedt [1]. In particular, it was suggested in that book that the success obtained in producing shear-refinement effects in *linear* polymers raised the issue of re-examining the concepts of entanglement and of visco-elasticity themselves, that is, the foundation of polymer rheology. In the following, "shear-refinement", "disentanglement" and "melt instability" will be used as synonyms, although a subtle difference between these terms exits as explained in [2].

One of the main issues of polymer science has been to balance the benefits of increasing the molecular weight of the macromolecular chains to improve the mechanical properties, and the disastrous impact of increasing the molecular weight on the processing ability, mostly because of the power 3.4 melt viscosity increase with molecular weight [26, 27]. The problems inherent to processing highly viscous melts are worsened by the introduction of additives and other compounds that are added to the resin to further improve the mechanical characteristics of the finished article or are necessary to avoid the chemical degradation of the chains by the high temperatures required to process them because of thehigh viscosity [31-34].

The effect of a "shear-refinement" or "melt disentanglement" mechanical pre-treatment results in a reversible substantial decrease of the melt viscosity and of its elasticity that can be controlled by the parameters of the pre-treatment. This melt pre-treatment may represent, therefore, a key solution to the dilemma of processing high viscous melts [27]. This says how much the question whether shear-refinement can be applied practically to linear polymer is an important issue!

In one hand, the paper by Münstedt [1] stated that the results presented for linear polymers in [2] were probably due to artifacts and not to shear-refinement, concluding that only branched polymers can be shear-refined. In the other hand, Ref. [2] summarized the work of several years that detailed new mechanical shear-pre-treatments of *linear* polymers (LLDPE, PC, PS, PMMA etc.) and concluded that the established molecular dynamic explanations of entanglement and visco-elasticity were challenged by these "disentanglement" results. The new mechanical pre-treatments used a combination of shear-thinning and strain softening means under vibration that produced substantially more shear-refinement effects than any previous method ever did. The clear contradiction between these two publications is examined in this communication.

II. Development

a) The misquotes of Münstedt's to disqualify that shear-refinement does not occur in linear polymers

Münstedt qualifies the important criteria to determine the success of a shear-refinement pre-treatment [1]:

"Two types of information are essential for a deeper understanding of the effects of mechanical pretreatments on the rheological behavior. First is the molecular structure of the polymer in its different states of pretreatment. Molar mass, molar mass distribution and branching architecture are the most important quantities. The second type of information relates to rheological properties. These must be well defined and accurately measured."

One of the criteria of success demonstrated by shear-refinement is specifically claimed by a reduction of the melt viscosity after the pre-treatment. This is the 2ndcriteria referred to by Münstedt, "the rheological properties". Yet, the 1stcriteria, "the molar mass... and branching architecture", is also required to qualify whether shear-refinement is real or is due to the degradation of the chains. It is well known that mechanically processed polymer melts at high temperatures, such as in extrusion, are subject to thermal degradation, inducing a reduction of the molecular weight, hence of the viscosity, especially for entangled polymers.

It is clear, therefore, that if a reader is exposed to shear-refinement results and the information is not given concerning the change of molecular weight, or the MWD was not even carried out, the reader should be inclined to disqualify the conclusions drawn from these results. As will be shown below, Münstedt mentioned such arguments in his paper against the credibility of the shear-refinement results for linear polymers [1]. But such quotes were not genuine.

In reality, great details about the procedures used for the shear-refinement experiments appeared in [2]: the equipment, the possible pitfalls, the shortcomings and how to avoid or get rid of them (p. 116-122 section 4.2, section 4.4.2.6, section 4.16 p.113, p. 216, section 4.4.2 "challenging interpretations, p. 211 of [1]).

Additionally, Refs. [2, 3] were both devoted to describe how the 1st criteria elected by Münstedt was made effective: how two Gel Permeation

Chromatography instruments (GPC by Waters Instruments Inc.) worked around the clock testing all the samples collected, systematically comparing their MWD with the Virgin reference's, for each batch, how the ratio of (Mw/MwRef.)3.4 was used to correct the viscosity results for that same treated sample. Overall, how more than 13,500 samples of linear polymers were "shear-refine-processed" and tested rheologically and their MWD used to correct the viscosity results [2,3].

Münstedt stated in the abstract of [1], summarizing his conclusions, that when the pre-treatment is real and not due to chain degradation, "it is obvious" that the polymer can only be a long chain branched polymer. He therefore asserted, after reviewing the shear-refinement data on linear polymers presented in [2], that their shear-refinement was not conclusive, i.e. that the apparent reduction of viscosity observed was due to either chain degradation or due to artifacts. This rebuttal is written to confront these statements.

In the following we show that some statements backing Münstedt's assertions misquote or misrepresent the work reported in the book by claiming things which are false or become false by intentional omission of the necessary details required to understand the results. The questionable statements are numbered from 1 to 7 and the objected part are underlined and in bold character.

1. *A commercial LLDPE (ethylene/octene elastomer with Mw=170 kg/mol and Mn=90 kg/mol) was subjected to a strong mechanical pretreatment in the sophisticated device described in [14]. A decrease of Mw was mentioned, but data were not reported.*

   Rebuttal: book Ch. 2, Table 2.1, 3rdrow " LLDPE". The Table parameters regarding molecular degradation are described at p. 26. This table provides the MFI of the untreated and of the pre-treated samples and it is explained that the raw MFI value is corrected for the effect of molecular weight degradation (2 to 5% at p. 26) to obtain the "flow improvement" value, the excess viscosity improvement not due to degradation (the part due to "shear-refinement"). The same type of results are discussed for Polycarbonate at Table 4.1 p. 238 with the note below the Table explaining how GPC measurements before and after the treatment permit to determine the MFI correction due to chain degradation. Additionally, Münstedt was sent by email the GPC curves for LLDPE before and after the pre-treatment [3].

2. In Appendix B of [1]: Polymethylmethacrylate *Modifications of another linear polymer exposed to intensive mechanical pretreatments are described in [14]. For a PMMA random copolymer of 95 % methylmethacrylate and 5 % ethylacrylate with M_w=78 kg/mol and M_n=40 kg/mol, a decrease of the viscosity measured in a dynamic-mechanical experiment after mechanical pretreatment in a special extrusion device was observed. At a first glance, this result might be explained by a thermomechanically induced degradation of the PMMA that would reduce viscosity. It was reported, however, that the initial viscosity curve was approached again when the material was annealed for 24 h at 215°C. This reversibility is taken as an argument for the existence of a pretreatment effect and the absence of a molar mass reduction, which would be, of course, irreversible. However, an analysis of the molecular structure was not carried out.*

   Rebuttal: Ch. 2, Table 2.1 row 5 ("PMMA"): The MFI flow improvement AFTER GPC correction for the change of M_w for this PMMA grade (MFI=17) is 117% . The % degradation of Mw is at p. 26 : "Yet, the molecular weight was hardly changed(~3%) to justify the viscosity reduction(117%)…". Also lines 1-11 at p. 212, for PMMA ("degradation was between 1 -5% depending on the extent of disentanglement obtained).

3. In Appendix B of [1]: Polycarbonate and polystyrene *Polystyrene and polycarbonate are two other linear polymeric materials, which have been discussed in [14]. They were mechanically pretreated in the sophisticated extrusion device described there or by oscillations at high amplitudes in plate-plate geometries. For the two polymers, pretreatment effects have been reported. They were interpreted by a model based on a new theory of polymer physics postulated in [14]. The results have to be considered with some reservation insofar as comparable studies on polycarbonate and polystyrene have not been published in the literature up to now. Furthermore, two questions related to the performance of the experiments would need to be addressed in more detail. The one concerns an undisturbed flow field at the high amplitudes or shear rates used in the plate-plate geometry as discussed in Appendix A. This topic is only tackled indirectly by making use of theoretical considerations from the literature, but direct visual observations of the sample geometry are not shown. The other point is the lack of a convincing molecular analysis in order to demonstrate that the molar mass distribution remained the same during the various steps of pretreatment and recovery of the samples.*

   Rebuttal: For PS and PC, see Table 2.1 p. 27: row 5 for PMMA, row 1 for PC. The MFI flow improvement AFTER GPC correction for the change of M_w is 75% for PC for this PC grade (MFI=12), and 50% for PS. The MWD obtained by GPC before and after treatment is shown in Fig. 4.6 at p. 213 and discussed in p. 212. Table 4.1 at p. 238 gives the % flow increase for several treated PC samples and defines how to calculate the % flow improvement (shear-refinement) from GPC results.

4. at p. 21 of [1]: *For example, comparing the frequencies and amplitudes chosen in [14] for measurements on PS, which are discussed in Appendix B, with the results in [45], it is evident that edge fracture and its recovery must be considered as sources for the rheological behavior observed, and, thus, any conclusions with respect to effects of mechanical pretreatment and their recovery may be drawn with particular care. No visual observations have been reported to show that geometrical disturbances did not occur during the experiments.*

   Rebuttal: 1. the experiments of [45] by Friedrich are discussed in the book in Ch. 4 (they are refs 60, 61 of ch.4). "Edge fracture explanation" at section 4.4.2.6., p. 216. Also Melt Fracture in parallel plate experiments is covered in section 4.16, at p. 113.
5. at p. 21 of [1] (continued):*These results demonstrate that plate-plate rheometry may not be a suitable method for studies of the effect of a mechanical pretreatment on rheological properties. To exclude geometrical artefacts during oscillatory experiments or measurements at constant shear rates, visual observations are necessary, which are not easy to perform.*

   Rebuttal: All the possible challenging explanations for the shear-refinements results of the book are discussed in section 4.4.2 p. 211 sq.

The best way to prove that artifacts are not involved during oscillatory experiments or measurements at constant shear rate in plate plate geometry is not a visual observation of the surface (which is ,indeed, "not easy to perform" and, besides, turns out to be non conclusive). The best proof is to compare the plate-plate rheological results of viscosity, which are "simulation experiments" results in a rheometer, with the "real" experiments viscosity results on the same sample using the same conditions (with the exception of the extrusion shear rate which is experimentally added but remains constant). This difference between real experiments and simulated experiments in the lab is not acknowledged by Münstedt who does the amalgam, as developed below, and this results in false conclusions. In"real" experiments, the viscosity is measured in the processing chamber designed to separately perform the pre-shearing treatment, and it is measured by an in-line viscometer located at the exit of the melt. In the case of real experiments, the continuous flow of the polymer in a confined gap occurs without edge fracture problems. Additionally, means are added to avoid melt slippage, ensuring a very smooth melt. Therefore, when the effect of frequency and strain amplitude trigger the same rheological response in both the simulated and the real experiments (section 2.2 , p. 22-25, Figs. 2.1 to 2.6 and section 4.1.5.2 p.100 and Fig. 4.5), this is the best proof that the melt instability effect is real. In addition, the pellets obtained by granulation of the frozen strands exiting the die can be measured rheologically under conditions of linear viscoelastic behavior, like for untreated pellets, and the recovery of the viscosity for the treated samples can be spectacularly observed in a plate-plate rheometer, with no possible artifact reasons attributed to the viscosity increase (Figs. 4.33, 4.50, 4.55 etc.)

6. at p. 21 of [1] (continued):*In any case, a broader experimental base of studies by several authors, which should be comparable to each other, is required for answering the question whether a mechanical pretreatment effect may occur for the linear polycarbonate or polystyrene in contrast to the results on the linear polypropylene reported above and those on linear polyethylenes from the literature.*

   Rebuttal: Why compare polycarbonate and polystyrene with polypropylene to validate the results obtained for PC and PS?. Each polymer has its own Rheo-Fluidification specifics. The obvious difference is their polarizability, polyolefins being non polar. The pre-treatment mechanical history parameters must account for the distinct response of different polymers to a shear-deformation to induce the melt instability. This is the know-how of the process.

   Indeed, "*a broader experimental base of studies by several authors…*" is desirable, but this will happen when reviews such as the one by influential scientists will cease denying the reality of the facts. The spread of tendentious opinions does not incite the financing of such important experimental work for the industry. See the section below:"The relunctance to change paradigms".

   Besides, the "disentanglement" experimental work that is summarized in the book has been validated and published by several teams of academics around China, including at the State Key Laboratory of Polymer Materials Engineering, College of Polymer Science and Engineering, Chengdu, Sichuan University [44, 45-48].

b) *The confusion generated by amalgamating the different sorts of mechanical pre-treatments*

There are several types of "pre-treatments" reported in the book [2], although Münstedt, in his review of the literature [1], does not mention this distinction. Yet, these different procedures to "treat the melt" are of critical importance to conclude whether the results are validating the presence of shear-refinement or are artifacts.

i. *The "real" treatments.*

These are the treatments that are applied via an extruder, a twin-screw, or the machinery that is described in [2] that Münstedt reports in such terms: " *Commercial products were subjected to intensive* *mechanical deformations combining shear, elongation and even oscillations in an especially designed extrusion device*”. This device is named a “Rheo-Fluidizer” ([2], Ch. 2, Ch. 4 p. 101, [27]). Another shear-refinement pre-treatment device is the “Rheo-Plast”, designed by Agassant and co-workers of CEMEF [41] and applied by Bourrigaud in his thesis [42]. The corresponding paper is quoted by Münstedt (Ref. 39 of [1]). Interestingly, the Rheo-Plast has been used by Agassant [41] to obtain significant shear-refinement improvements for a linear Polyvinyl chloride (PVC), although this result, not discussed by Münstedt, appears to be in contradiction with his own conclusions.

The common feature of all these pre-treatment equipments is that the melt is treated ahead and/or separately of/from the processing unit that exits the melt, allowing to measure the melt viscosity both in the pre-treatment processing unit and via an on-line viscometer positioned at the exit. The meltcan also exit the pre-treatment processing unit through an exit die to create strands that are water quenched and pelletized. Subsequently the pellets can be studied to measure their molecular structure and their rheological properties. In all of these “real” treatments of the melt, the melt is confined in a circular gap with no edge effect. The melt is either extruded while being cross-sheared in the direction perpendicular to the flow axis, or it is simply cross-sheared by rotation of the bob inside the barrel, but not extruded through, alike in a Couette type of rheometer geometry.

The distinctive feature between all the equipment described in the literature as “Shear-Refinement equipment” and the “Rheo-Fluidification” processors reported in [2, 36-40]is the use of melt vibration means to modify the melt rheological properties in addition to the traditional shear and pressure means [27]. This distinctive feature is critical to obtain the melt instability results that are described in the book and in many other communications (Ref. [15] of Ch.2 of [2] provides a list).

ii. *The “simulation” treatments*

These pre-treatments are done in a laboratory rheometer using the plate-plate or the cone-plate configuration. The melt is gently squeezed between the two circular plates but is not confined, presenting an open surface at the rim of the disk. This work is called a “simulation treatment” because it does not reproduce the real treatment conditions of the confined treated melts which don’t have edge effects problems. However, even if the variation of the frequency and of the strain amplitude must be restricted to the range whether no melt fracture occurs at the edge, the “simulation experiments” provide important rheological results that are validated when those compare well with the rheological behavior observed for the “real” experiments that they are supposed to simulate.

iii. *The crucial difference between “in-line disentanglement” and “in-pellet disentanglement”*

Ref. [2] emphasizes a great deal the difference between these two types of pre-treatment achievements. The degree of difficulty in achieving one or the other is really crucial for its industrial impact but Münstedt simply ignored this issue.

The conclusions of the “disentanglement” work (Chs. 2,7, 8 of [2]) can be simplified and summarized as follows:

- It is straightforward to achieve for linear polymers huge “disentanglement” benefits (thousand percent decrease of viscosity etc.) when using Rheo-Fluidizers as on-line melt pre-treatment devices. The Rheo-Fluidizer chamber must be positioned ahead of the application requiring the feed of a molten “disentangled” melt. Pressure decrease, temperature decrease, torque decrease are spectacularly lower for all the polymers experimented with (about adozen), as reported in [2]. The optimum conditions are easy to find. Because of the use of much lower temperature to process melt under Rheo-Fluidification condition (e.g. for PC. 235°C instead of 315°C), thermal degradation is also reduced compared to normal extrusion. The results can be understood by considerations of shear-thinning and strain softening expressed in terms of the Dual-Phase model (Ch.5 of [2]).
- To have achieved substantial “in-pellet disentanglement” for at least 5 polymers (Table 2.1 of [2]) was much more challenging to do. Its theoretical implication, as suggested in the book, necessitates a change of paradigm in understanding the physics of interactions in polymers. This is why the “in-pellet disentanglement” results, designated “sustained-Orientation”, are exposed in the first chapter of the book after the Preamble: “*Trouble with Polymer Physics: Sustained-Orientation. Ground-Breaking Experimental Research Shakes the Current Understanding of the Liquid State of Polymers*” (p. 21-30).

Münstedt, makes an amagalm of the pre-treatments results, whether produced by a real treatment or a simulated treatment, whether it is an in-line disentanglement or an in-pellet disentanglement achievement, and this confusion is unacceptable to assess (and disqualify) the ability of linear polymers to shear-refine.

7. At p.23 of [1],: *The ability to reversibly modify LLDPE by a mechanical pretreatment was claimed to be supported by the following experiment using plate-plate geometry [14]. After an oscillation at the angular frequency of $\omega=0.1$ rad/s and the strain amplitude of $\gamma0=1\%$ in the linear regime, the amplitude was stepwise increased up to an amplitude of 25 % at a frequency of 47 rad/s. Due to its frequency*

dependence, the viscosity decreased by a factor of six and went down further by a factor of two during the 25 min of high amplitude oscillations. Then using the initial linear conditions again, the viscosity rose and regained its starting plateau after about 10 min. This behavior was interpreted as a recoverable shear modification of the LLDPE at the amplitudes and the frequency in the nonlinear regime. These conclusions have to be considered, however, with some reservation in the light of Appendix A, where the results of other authors have been discussed, who performed similar experiments in plate-plate rheometers and reported a decrease of the complex moduli with time at high amplitudes for PP [44] and PS [45] but showed that this behavior was accompanied by sample fracture during the experiment.

8. *Rebuttal:* The plate-plate dynamic experiments reported above on LLDPE (Engage 8180 of Dupont-Dow Elastomers) are taken from Figs. 4.28 and 4.29 of [2]. They are actually repeats done in the laboratory of L.A. Utracki in Montreal (IMI, Boucherville, CA) of tests conducted a few years before that at McGill University with a PhD student of J. Dealy, under his supervision. They represent "simulation" experiments done with a plate-plate dynamic rheometer. Other simulation experiments were done on this LLDPE: pure viscometry tests reported in Fig. 4.2, 4.15 to 4.22 of [2], and viscometry followed by frequency tests in Figs. 4.23 to 4.25 of [2]. All these simulation experiments concur with the triggering of the time dependence of the viscosity but they do not, indeed, say that plate-plate geometry does not influence the results observed. One could say that the level of confidence that the time-dependence of viscosity triggered by a modulated strain increase (Fig. 4.28 b of [2]) was real and not caused by an artifact was around 90% at the time. A few years later, to raise the level of confidence to 100%, the 1st Rheo-Fluidizer processor was designed and built [26, 27, Ch. 2 of [2]]. The same LLDPE resin used earlier at McGill and IMI was treated in the Rheo-Fluidizing processor to produce all kinds of pre-treatments: in-line disentanglement: Figs. 4.6, 4.26 of [2], or in-pellets disentanglement (Ch. 2, Table 2.1 of [2]). These "real" experiments provided rheological results (Figs. 4.7 a and b of [2]) qualitatively identical to those obtained by the plate-plate "simulated" experiments, either by pure viscometry or by dynamic rheometry. In summary, Münstedt draws an objectionable conclusion by comparing the work of others ([44], [45]) who are using different materials than LLDPE, and by not comparing plate-plate "simulations" and "real experiments" reported in dozens of figures for this polymer in the book.

c) *Misrepresentation by omission*

Something is certain that is not reported by Münstedt, although it is a critical part of the book: the time dependence of viscosity triggered by an increase of the shear strain occurs above a critical strain that is rather small (25% to 50%) and not like the 300% strain quoted by Münstedt that causes the fracture of the melt that is wrongly compared to our results in his Appendix A. Besides, and it is fundamental to say this, the time dependence of viscosity triggered under shear-thinning conditions at low critical strain is observed for both confined melts, even while being extruded, and for melts studied in a plate-plate open edge rheometer. Even if edge effects would induce the time dependence seen in the open edge experiment, this could not be the reason for the shear-induced time dependence when there is no edge! Furthermore, the pellets granulated after the melt viscosity has been reduced by the pre-treatment exhibit a melt flow index that is totally correlated to the pre-treatment viscosity value measured in the Rheo-Fluidizing processing unit (see Figs. 2.6, p.25, 4.9 p. 120, and 4.74 p. 231 in [2]). This was not an anecdotic phenomenon: Ref. [2] reports that 150 lbs lots of "disentangled" polycarbonate and of PMMA were produced and distributed to the large resin manufacturing companies of the world (in Germany, US, Japan and France) who endorsed the results and signed license agreements. Omitting to report this essential evidence appears to insinuate that no one has been able to repeat the work of "disentanglement" described in the book.

By calling "shear-refinement" the "disentanglement" work published in [2], Münstedt omitted to explain, even in a few lines, the basic principles behind "Rheo-Fluidification" and how it differentiated with the prior art, precisely with shear-refinement, making the comparison between the respective results objectable in his paper[1].

In Rheo-Fluidification, unlike in any previous practice of shear-refinement, the shear rate is the vector combination of 3 shear rates that can be controlled independently: a pressure flow shear rate controlled by the extrusion parameters, a cross-lateral shear rate controlled by the RPM of the core shaft inside the treatment chamber, and, superposed onto this cross-lateral shear-rate, a shear rate due to the vibration of the melt in the gap by means that control its frequency and amplitude. The objective of Rheo-Fluidification is to impose to the melt a specific rheological treatment composed of a mix of shear-thinning and strain softening to induce the temporary instability of the rheology of the interactions that create the melt cohesion(from which derive its visco-elastic properties, e.g. the G' and G" components of the modulus).

These specific hybrid shear-thinning/ strain softening mechanical treatments have never been applied by the prior art to polymer melts, neither as pre-treatments or during processing. While many problems subsist to improve the efficiency of the Rheo-Fluidizing processes (Ch. 8 of [2]), what has become unquestionable is their ability to substantially reduce the in-line processing parameters when processing those melts, allowing, for instance, to work at either much lower torque (2 to 10 times less), lower temperature (-50 to -100 oC less) or under much lower pressures for the same throughput. Ref. [2] describes these important benefits to processors as the "in-line Rheo-Fluidification benefits". Questioning those results, as it is hinted explicitly or implicitly in Ref. [1], by saying that they should be taken with some caution because they probably are due to degradation, or because the author did not mention or measure the molecular characteristics of the treated melt, is deceptively wrong.

Münstedt omits to mention that the book provides a full assessment of shear-refinement (section 4.1.5.2.3 p. 110-116) and that it addresses the classically admitted argument (revived in his article) that Shear-Refinement only works for branched polymers, being useless for linear polymers, a restriction that has limited the range of applications and the spread of this technology.

Münstedt, omits to mention:

- That Rheo-Fluidification intentionally experimented with a variation of Shear-Refinement because it combines, under vibration, shear-thinning and strain softening effects on the melt to induce a temporary state of rheological instability.
- That this non-equilibrium state of the melt could be controlled by changing the rheological parameters in the Rheo-Fluidizing processor.
- That the Rheo-Fluidified melt could be extruded to provide pellets presenting controlled higher melt flow indexes (MFI) or that it could be placed ahead of a classical processing operation such as an extrusion or an injection molding.
- That the temporary rheological instability of the melt could be obtained with either linear or branched polymers.

d) Münstedt 's Critical Condition that Branching must be Present to Observe Shear-Refinement is Wrong

In the book [2], we introduce new equations to analyze the rheology of melts (shear-thinning, strain-softening) in terms of the Dual-Phase model and show that they also explain the origin of the rheological instability. The long term retention of the lower viscosity in the Rheo-fluidified pellets when re-heated to a melt state, sometimes for times several hundred thousand times greater than the reptation time at that temperature, represents an immense challenge to the currently admitted models of chain dynamics such as reptation. This challenge is not acknowledged by the community of rheologists, except swept away as artifact, such as in the paper by Münstedt. However, how could this be an artifact when we did produce several lots of 150 lbs of sustained-oriented pellets, the product of the "artifact", which could regain in time their original viscosity after re-melting!

The "Sustained Orientation" paradox is linked to a new concept: the instability of the Dual-Phase of the interactions (Ch. 2 of [2]). A first degree instability can be induced by a combination of shear-thinning and strain softening that may result in shear-refinement effects. Sustained-Orientation requires certain conditions in addition to the 1st degree instability criteria to trigger an instability of the 2nd kind: the instability of the entanglement structure.

It is shown that there are two types of sources to trigger the rheological instabilities of polymer melts: one is controlled by the recoverable dynamic free volume variations, the other by the modification of the entanglement network structure, by entropic dissipation (orientation of the network). This dilemma between which mechanism of instability dominates for a given polymer is the true debate to have regarding the shear-refinement results. For instance, the Dual-Phase model of the interactions (Ch. 1 of [2]) explains the dynamic source of the free volume (the F-conformers)which is also influenced by the topology of the chains, in particular whether long chain branching, short chain branching or no branching is present. Both the amount and the structure of the dynamic free volume is influenced by branching. But the dynamic free volume is also influenced by other rheological factors: the orientation of the chains, the frequency and the amplitude of a vibration of the coherent interactive medium, the pressure in the melt, etc. All these parameters influence the local density of the melt and the frequency of the elastic dissipative wave that compensates for the local packing density in-homogeneity between the b and F conformers. In turn, they also influence the melt modulus (the famous G= ρRT/M correlation), and thus influence shear-thinning and strain softening. Münstedt focuses on the presence of the long chain branches to determine a criteria for shear-refinement [1]. This focus is lacking crucial information which are not given by the molecular models: 1.the determination of the local packing density and of the location of the free volume in the structure, and 2. the influence of branching on these two variables. The Dual-Phase model is easily applicable to this situation because of the cross-duality between the F/b dissipative states and the conformational states (trans, cis, gauche). This [(F/b) ←-→ (c,g,t)] cross-duality also predicts the influence of vibration, shear rate and shear strain on the free volume amount and its distribution, in particular how to increase it, whether the basic polymer is branched or linear. Therefore, the topological criteria by Münstedt that branching must be present to observe the conditions for shear-refinement is simply wrong. The correlation must be established with the amount and structure of the dynamic free volume instead.

e) The question and the reluctance of the need to change Paradigms

Admittedly, the apparent disagreement between two scientists on the interpretation of shear-refinement, whether the polymer chains must be branched or can be linear, only touches the visible part of the iceberg. In fact, the real controversy was not about shear-refinement, it was about the need to change paradigm to understand all aspects of visco-elasticity, including shear-refinement. If shear-refinement benefits do apply to linear chain polymers, is our current understanding of the physics of polymers, specifically the concept of entanglement, in default? If the current dynamic molecular models of rheology are incomplete to explain certain linear and non-linear rheological experiments of polymer melts (Chs. 6 and 7 of [2]), should we not change paradigm to explain interactions in polymers?

During the ten years of persistent and systematic experimental validation of the evidence regarding "sustained-orientation" that was revealed through publications at annual APS and SPE meetings [4-25] and in patent letters [26-34], it became apparent that these results appeared to conflict with the established models of melt deformation. This made this author decide to endorse a full academic career to concentrate on the understanding of "sustained-orientation" and "entanglements". The book in Ref. [2] is the first result from that effort (Ch. 8). More publications are in the works ([51. 52]).

f) A few words about the new Paradigm

In our view, "conformers", the constituents of the macromolecules, gather into statistical systems which go beyond belonging to individual macromolecules. A conformer is shown in Figure 1.1 of Ch. 1 of [2]. The macromolecules themselves represent a chain of "covalent conformers" put together as an entity. The problem is to determine whether the chain properties, derived from its statistics, control entirely the dynamics of the collection of chains making up a polymer. This is what has been assumed by all the other theories, and this is what the Dual-Split kinetics and the Grain-Field statistics challenge.

Also in our model of interactions, the Free energy of the collection of chains assembled as a polymer is not equal to the scaled-up Free energy of a macromolecule embedded in a mean field created by the influence of the other macromolecules. This is particularly true below the temperature T_{LL} (see below), which itself is function of the dynamics of the experiment and the chain characteristics. In fact, for many experimental conditions, depending on temperature and other factors, our model of polymer interactions does not require, in its hypotheses and derivations, a description of the changes which occur to the individual macromolecules (like its rms end-to-end distance). The dynamic statistical systems dealt with to determine the Free energy and its structure (Enthalpy and Entropy), are not the macromolecules in our approach. However, the fact that macromolecules compose the basic structure is essential, for instance to understand the basis of our new Dual-Phase statistics and to explain "entanglements", for which our model provides a completely different interpretation than the ones offered by the conventional spaghetti bowl or tube models [Ch.1 of [2]].

A "covalent conformer" is not the same as a "free conformer", often seen as the three-bond element constituting the mer in the polymerization process. Its interaction to other conformers by covalent bonding modifies the conformational potential energyof a free conformer, and this governs the statistical properties of a "free chain". Here we are still "classical", yet when dealing with a collection of chains put together, our approach differs from the classical one. Conformers belong to two types of sets: they belong to macromolecules, which link them via covalent forces, as we just said, and they belong to the grand ensemble of conformers which are linked by inter-intra molecular forces, van der Waals, dipole-dipole, and electrostatic interactions which affect and define the viscous medium. That duality is intrinsic to conformers, which are thus called "the dual-conformers" to mark this specificity. The potential energy of a dual-conformer is different from the potential energy of a conformer part of a free chain.

To simplify, one could view the difference between our statistical model and the classical model to describe the properties of polymers as follows: according to the classical views, the statistical systems are the macromolecules, i.e. a network of chains; the properties of the chains are disturbed by the presence of other chains and by the external conditions (temperature, stress tensor, electrical field, etc.). The classical definition of the statistical system contrasts with our approach whereby the statistical systems are the "dual-conformers", not the macromolecules. The interactive coupling between the dual-conformers is defined by a new statistics, the Grain-Field Statistics, that explores the correlation between the local conformational property of the dual-conformers and their collective behavior as a dissipative network (we designate below the dual-conformers "conformers", to simplify).

The statistics that are used by the classical models and by our model to describe the RIS (rotational isomeric states) of the conformers are fundamentally different: the classical molecular dynamic statistics is the Boltzmann statistics, famous for its kinetic formulation of the properties of gases. The Dual-Split or Dual-Phase statistics, leading to the Grain-Field Statistics, is inspired by the classical Boltzmann concept but departs from it by defining a dissipative term in the RIS equations and assuming that the Free Energy remains always equal to its minimum value, that of the equilibrium state, even for transient states. The dynamics created by such changes in the fundamental equations result in the formation of a collective modulation responsible in rheology for the "the elastic dissipative wave" to compensate for the local dynamic free volume difference between the F and b conformers (Ch. 1 of [2]).

In our analytical formulation of the dynamics of these "open dissipative systems of interactions" generated by our two modifications of the classical formula, we realized that essentially two mechanisms of structuration of the Free Energy prevailed and competed: a "vertical structuring" and a "horizontal" structuring", each specifically applying its own version of the basic equations. This distinction increased the complexity of the analytical solution but was, in our opinion, a fundamental aspect of the way interactions worked. The vertical structuring refered to a split of the units (collectively interacting in the system) into 2 compensating sub-systems having each a different statistical partition. The horizontal structuring, also called "cloning", offered a different split of the collective set, via the generation of Ns identical sub-systems, each with the same statistical partition. Each split mechanism generated a dissipative function. The total dissipative function ought to be minimized (it is 0 at stable equilibrium), a condition that created their mode of compensation, i.e. whether they worked independently, in sequence or simultaneously.

These general principles can be applied to describe the rheology (linear and non-linear) of polymer melts, define the entanglement network and quantify its stability.

g) The T_{LL} transition

The details of the simulations performed using the Grain-Field model of polymer interactions shows the existence of a temperature, that we associate with T_{LL}, where the collective modulation of the local interactions between conformers by the open dissipative network collapses. A recent two-parts article [43] explores the properties of T_{LL} when it is defined in such a manner. It is shown that T_{LL} plays a crucial role in deciding whether and when the Boltzmann's statistical theory is allowed to be used to determine the status of the interactions when a stress or a voltage field is applied [43]. T_{LL} appears as the temperature of transition between these two assessments of the interactions: below T_{LL}, the collective dissipative aspect of the interactions dominates, i.e. the statistical systems of interactions are open dynamic systems that are not the macromolecules, and the energy of the interactions as a whole modulates the local conformational states: the Boltzmann's statistics does not apply. Above T_{LL}, however, the collective modulation collapses, the statistical systems are no longer dissipative and the Grain-Field statistics becomes the Boltzmann's statistics. The macromolecular chains could now be considered as Boltzmann's statistical interacting systems, as an alternative option to the Grain-Field statistics (that continues to be valid, though, even if it is no longer dissipative).

In our conclusions, this is a key issue: the currently established theoretical models of the interactions in polymers are based on "chain dynamics" statistics. In rheology, for instance, the Rouse and reptation models explain most of the behavior for $M < Mc$ and $M > Mc$, respectively. But these models fail to explain "Sustained-Orientation" and "T_{LL}" and other non-linear properties of polymers (Chs. 6 and 7 of [2]). The reason for this partial success of the classical models can be explained by the Grain-Field Statistics of the interactions which, as we just said, remains valid at all temperatures across T_{LL}, yet stops being dissipative and becomes coherent with the classical statistics used by the molecular dynamic models when $T > T_{LL}$. Consequently, the application of macromolecular (chain) dynamic models can only be justified for conditions of use of the material that position its temperature above the T_{LL} transition ($T > T_{LL}$). The problem is that the existence of T_{LL} is not even recognized by these molecular dynamic models. Below T_{LL}, the free energy of the collection of chains assembled as a polymer is not equal to the scaled-up free energy of a macromolecule embedded in a mean field created by the influence of the other macromolecules. Besides, the temperature T_{LL} is itself a function of the dynamics of the experiment and the chain characteristics.

If one tests the predictions of the classical approach under conditions that bring its state above T_{LL}, one may conclude that those data validate the classical views since they provide correct answers in the range tested. This is not an easy task, because T_{LL} is rate dependent, pressure and shear dependent and molecular weight dependent [43]. Thus, although one will find in the literature convincing experimental evidence of success for the classical models, which is the reason for their acceptance, we claim that these successes are due to the use of conditions that bring the state of the polymer above its T_{LL} transition. We have suggested abandoning the molecular dynamic interpretations of the behavior of polymer melts because of their lack of general applicability (Ch. 8 of [2], [51, 52]).

III. CONCLUSION

We show in this paper that Münstedt[1] has not been genuine in his quotations of our work [2] by incorrectly reporting the results and the procedures, by muting important details, and by making amalgams between different types of experiments to draw wrong conclusions that mislead more than inform the reader about the content of the work and its importance for polymer science and technology. The excuse that no one else has been carrying out similar experiments to be able to prove it or disprove it is wrong: many reputable academic institutions in China have duplicated our entanglement instability work reported in [2] and elsewhere [4-40], validating our results in recent publications [44-50].

We have addressed the following subjects and reported their importance in our publications:

- There is no good reason to doubt and attempt to disqualify the results on the shear-induced melt instability of linear polymers (designated "disentanglement" in Ch. 4 of [2]). Münstedt misquotes were corrected and their implications refuted.
- Münstedt used the classical topological description of long chain branched (LCB) polymers to support his opinion that linear chain polymers cannot qualify to successfully induce shear-refinement effects. We argued that although LCBs and linear chains are architecturally different, the true cause for shear-refinement must be found elsewhere, and we pointed to the dynamic free volume as one of the causes of the melt instability triggering a reduction of viscosity. LCB polymers have inherently more dynamic free volume than the linear polymers, but both architectures can support a substantial enhancement by melt Rheo-Fluidizing manipulation, not just the LCB type. The dynamic free volume is quantified by the Grain-Field Statistics model of the interactions but not by the molecular dynamic models.
- The reluctance to accept the "melt instability" experimental results by Münstedt was perhaps motivated by the lack of molecular dynamic models' arguments to comprehend these results (Chs. 6, 7 of [2]).
- The discovery of the instability of the entanglement network triggers the necessity to understand entanglements differently (Ch. 1, 2 of [2]).
- The debate brought by Münstedt whether linear polymers can trigger shear-refinement or not was the tip of the iceberg. The real debate concerns the validation of the Sustained-Orientation experiments and its impact to understand interactions in polymers, whether the macromolecules are themselves the statistical systems of interaction, the current view, or the source of a modification of a new statistics that renders dissipative the classical Boltzmann's formalism.

A recent review of our introductory book on the physics of polymer interactions has just been published by T. J. Hutley [53].This reviewer ends his review as follows:

"The broader and more extensive industrial implementation of disentanglement technology might be hindered by the complete paradigm shift introduced here. It requires a re-boot of the thinking of polymer engineering and the design of polymer processing equipment, which have all developed based upon an earlier rigid paradigm that polymers are necessarily high viscosity fluids.

The reviewer believes that achieving disentangled polymer melts is a new disruptive technology that could reconfigure the polymer industry value chain, and bring brand new economic and environmental (lower energy consumption) benefits. Bold engineers who can imagine the potential of what is described in this book will be on a path, along which few have travelled….."

While it is, indeed, crucial that scientists doubt the results of others and it is, of course, acceptable to disagree with someone else 's conclusions, the practice of deception, even subtly introduced, to refute what one disagrees with should remain a red line that is never crossed.

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