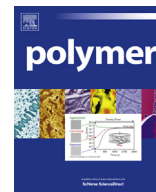




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# From linear viscoelasticity to elongational flow of polydisperse linear and branched polymer melts: The hierarchical multi-mode molecular stress function model

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Dedicated to the memory of **Victor Hugo Rolón-Garrido** (1979–2015).

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## ABSTRACT

We developed a novel Hierarchical Multi-mode Molecular Stress Function (HMMSF) model for polydisperse polymer melts, which implements the basic ideas of (i) hierarchical relaxation, (ii) dynamic dilution, and (iii) interchain tube pressure. Here, the capability of this approach is demonstrated by comparison of predictions of the HMMSF model with uniaxial extensional viscosity data of sixteen different grades of high and low density polyethylene melts, as well as two different polystyrene melts with defined topology. The modelling is solely based on the linear-viscoelastic relaxation modulus with only one non-linear material parameter, the dilution modulus.

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## 1. Introduction

The extent of the long-chain branching and molecular weight distribution of polymers has a significant impact on their rheological properties both in linear and non-linear viscoelastic regimes where the onset and strength of the strain hardening behaviour (i.e. deviation from the linear viscoelastic envelope) occur faster and more accentuated in long-chain branched (LCB) melts as opposed to linear melts subjected to extensional deformation. According to Lentzakis et al. (2013) [1], the microscopic responses of polymeric systems are directly reflective of their microstructural characteristics when their non-linear shear and extensional behaviours are significantly influenced by the long-chain branching and polydispersity. The dispersity of polymers is controlled through their synthesis mechanism, and the rheological characteristics of polymers are majorly controlled through their polydispersity as well as architecture (i.e. linear, H, pom-pom, comb, and Cayley tree architectures) [1].

The importance of the relationship between the molecular structure and rheological behaviour of polymeric systems is due to the considerable sensitivity of the rheological properties to the structural ones, as well as the principal role of the rheological characteristics in flow behaviour during the melt processing of the polymers [2]. The main obstacle in modelling the rheological behaviour is the ambiguity of the direct correlation between the molecular characteristics and the non-linear rheological responses. This obstacle is the result of the scarcity of experimental data of model polymers with well-defined topologies due to difficulties involved with the synthesis of these macromolecules, in addition to conducting measurements on miniscule amounts of well-defined samples [1]. Although the modelling of the polymerization reactions and melt forming operations could in principle result in the prediction of the detailed molecular structure of polymers and thus the prediction of the rheological properties based on the structure [2], this is not yet possible due to the large number of mostly unknown polymerization parameters in commercial operations.

The significance of the extensional rheological analysis of polymer melts is resulted from the subsection of nearly all polymer processing systems to extensional deformation at narrowing profile sections, where extensional flow dominates the rheological

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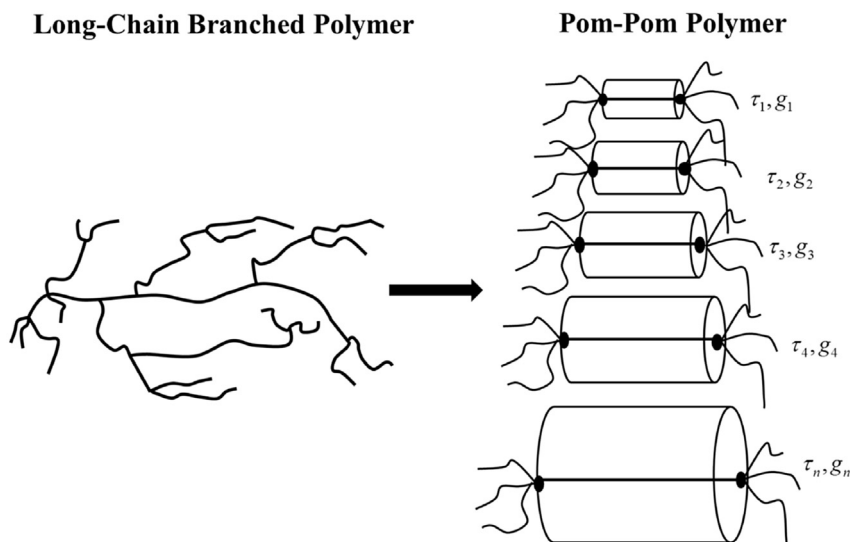


Fig. 1. Schematic representation of a long-chain branched polymer by a hierarchical series of pom-pom polymers with  $\tau_{i+1} > \tau_i$ . For details see text.

characteristics of the deformation [3–6]. This dominance is accentuated in processes such as blow moulding, melt spinning, and biaxial stretching of extruded sheets, and the extensional deformation may be the last step before solidification which triggers molecular orientation [7,8]. The occurrence of strain hardening behaviour prevents the formation of local weak spots as the starting point of cracks in plastic melts in free surface flows. Moreover, extensional deformations are very sensitive to macromolecular structure of the polymeric systems including degree of branching, molecular weight distribution, and cross-linking [8,9]. Both linear and branched polymers exhibit strain hardening. Strain hardening is markedly affected by the architecture of the polymers when the existence and abundance of branches as well as the number of the entanglements of the backbone directly impacts the strength and the onset of this rheological phenomenon.

In Narimissa et al. (2015a, 2016a,b) [10–12], we introduced a model which accurately predicts the uniaxial and multiaxial extensional as well as shear viscosity of several long-chain branched (LCB) polymer melts based exclusively on their linear-viscoelastic characterization, and features only a single non-linear material parameter, the dilution modulus  $G_D$ , for extensional flow, in addition to a constraint release parameter  $CR$  for shear flow. This Hierarchical Multi-mode Molecular Stress Function (HMMSF) model for LCB polymers implements the basic ideas of the pom-pom model, hierarchical relaxation, dynamic dilution and the interchain pressure.

In Narimissa and Wagner (2016) [13] we extended the HMMSF model to monodisperse, bidisperse, and polydisperse linear polymer melts by means of relating the relaxation times to the Rouse stretch-relaxation times for each mode.

The objective of this paper is to demonstrate the applicability of the HMMSF model to the elongational viscosity data of polydisperse linear and LCB polymers including metallocene-catalyzed polyethylenes, which consist of a mixture of linear and sparsely long-chain branched (star-shaped) macromolecules. The paper is organised as follows: We first give a short account of the concept of interchain pressure and dynamic dilution in constitutive modelling of linear monodisperse and bidisperse polymer melts, and then summarize the hierarchical multi-mode MSF model for polydisperse linear and LCB melts. The main part of the paper is devoted to the comparison of model predictions with experimental evidence of a multitude of linear and LCB polymers.

## 2. Theoretical background

### 2.1. The interchain tube pressure

Wagner and Schaeffer [14–16] proposed a generalized tube segment model with strain dependent tube diameter, i.e. the Molecular Stress Function (MSF) model. According to this model, the segmental chain stretch,  $f$ , is directly related to the diameter  $a$  of a tube segment. The tube diameter can be viewed as the mean field of

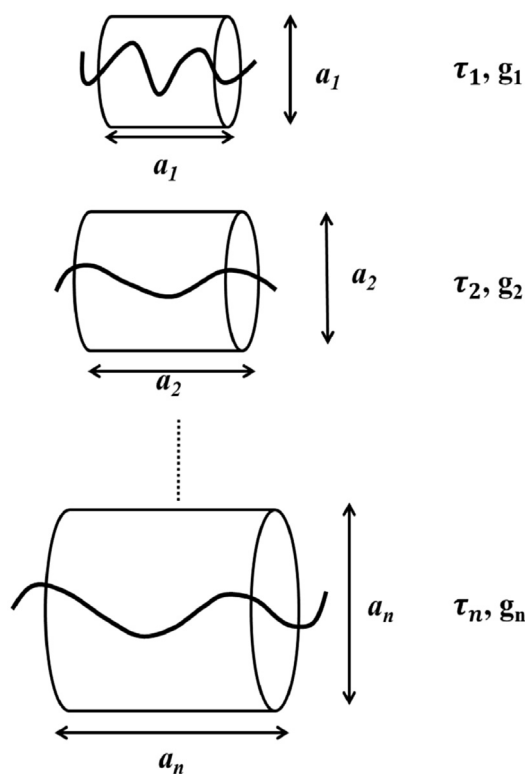


Fig. 2. Subdivision of an ensemble of polydisperse linear polymer chains into a series of hierarchically increasing tube diameter segments, characterized by increasing relaxation times; i.e.  $a_1 < a_2 < \dots < a_n$  and  $\tau_1 < \tau_2 < \dots < \tau_n$ . For details see text.

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