

CHARACTERIZATION OF METALLOCENE-CATALYZED POLYETHYLENES FROM RHEOLOGICAL MEASUREMENTS USING A BAYESIAN FORMULATION

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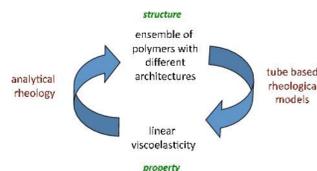


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Introduction

Long-chain branching affects the rheological properties of the polyethylenes strongly. Branching structure - density of branch points, branch length, and the locations of the branches - is complicated, therefore, without controlled branching structure it is almost impossible to study the effect of long-chain branching on the rheological properties. Single-site catalysts now make it possible to prepare samples in which the molecular weight distribution is relatively narrow and quite reproducible. In addition, a particular type of single-site catalyst, the constrained geometry catalyst, makes it possible to introduce low and well-controlled levels of long chain branching while keeping the molecular weight distribution narrow.

Linear viscoelastic properties (LVE) of rheological properties contain a rich amount of data regarding molecular structure of the polymers. A computational algorithm that seeks to invert the linear viscoelastic spectrum of single-site metallocene-catalyzed polyethylenes is presented in this work. The algorithm uses a general linear rheological model of branched polymers as its underlying engine, and is based on a Bayesian formulation that transforms the inverse problem into a sampling problem. Given experimental rheological data on unknown single-site metallocene-catalyzed polyethylenes, it is able to quantitatively describe the range of values of weight-averaged molecular weight, M_w , and average branching density, b_m , consistent with the data. The algorithm uses a Markov-chain Monte Carlo method to simulate the sampling problem. If, and when information about the molecular weight is available through supplementary experiments, such as chromatography or light scattering, it can easily be incorporated into the algorithm, as demonstrated.



Rheology

Rheology seeks to describe the flow behavior of materials using constitutive equations between stress and strain. Polymers lie between two extreme states, pure viscous and pure elastic, they represent properties of both of these two extremes, which is the reason we call them viscoelastic materials. Rheology is described by two regimes, linear and non-linear. Non-linear rheology refers to processes that involve large deformations that usually happen in industrial applications. Linear rheology (linear viscoelasticity) refers to processes that are in the vicinity of small deformations. In linear viscoelastic regime, constitutive equations (relationship between generated stress and related time derivatives to applied deformation) are in a linear form. Linear viscoelasticity is important in characterization of polymers, as it is very sensitive to structural properties of polymers. It can be used to extract the molecular weight and branching data information. Analytical rheology refers to using linear viscoelasticity data to infer the structural information of polymers.

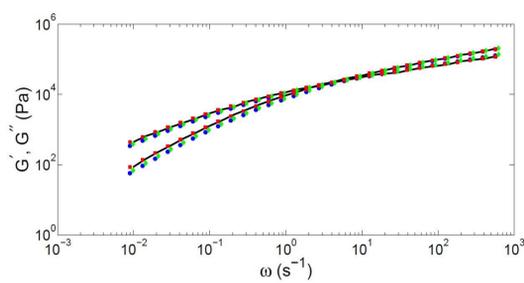


Figure 1: Linear Visco-elastic data for HDB 7

Polymerization Kinetics

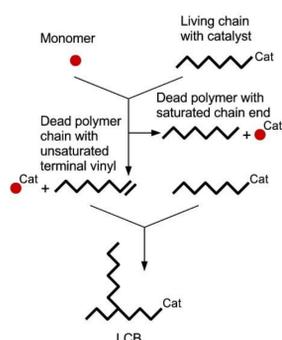


Figure 2: Reaction path for formation of LCB metallocene-polyethylene

Bayesian Formulation

As the forward model, the branch-on-branch model (BoB) of Das et al. is used. For mPE, BoB accepts two-parameter inputs as a two-state vector.

Structure Space: $\bar{\theta} = \{M_w, b_m\}$

Cost function: $\epsilon(\bar{\theta}) = \|\mathbf{d} - \mathbf{m}(\bar{\theta})\|$

$$\epsilon(\bar{\theta}) = \frac{1}{2} \sum \left(\log \frac{G'(\omega)}{G'_{exp}(\omega)} \right)^2 + \frac{1}{2} \sum \left(\log \frac{G''(\omega)}{G''_{exp}(\omega)} \right)^2$$

Likelihood function: $\pi(\mathbf{d}|\bar{\theta}) = e^{-\alpha\epsilon(\bar{\theta})}$

Prior Probabilities: - LVE: $\pi(\bar{\theta}) \sim 1$ - LVE+M: $\pi(\bar{\theta}) \sim \delta(M_w - M_w^{exp})$

Posterior Probability: $\pi(\bar{\theta}|\mathbf{d}) = \frac{\pi(\mathbf{d}|\bar{\theta})\pi(\bar{\theta})}{\sum_{\bar{\theta}} \pi(\mathbf{d}|\bar{\theta})\pi(\bar{\theta})}$

MCMC Algorithm

- LVE: $\bar{\theta} = \{M_w, b_m\}$, $\bar{\theta}' = \{M'_w, b'_m\}$
 $M'_w = \beta M_w$
 $b'_m = b_m + U(-\Delta b_m, \Delta b_m)$
 $\text{acc}(\bar{\theta} \rightarrow \bar{\theta}') = \beta e^{-\alpha[\epsilon(\bar{\theta}') - \epsilon(\bar{\theta})]}$

- LVE + M: $\bar{\theta} = \{M_w^{exp}, b_m\}$, $\bar{\theta}' = \{M_w^{exp}, b'_m\}$
 $b'_m = b_m + U(-\Delta b_m, \Delta b_m)$
 $\text{acc}(\bar{\theta} \rightarrow \bar{\theta}') = e^{-\alpha[\epsilon(\bar{\theta}') - \epsilon(\bar{\theta})]}$

Results

-LVE

- 20 Independent runs of MCS
- Top 75th percentile of data are considered

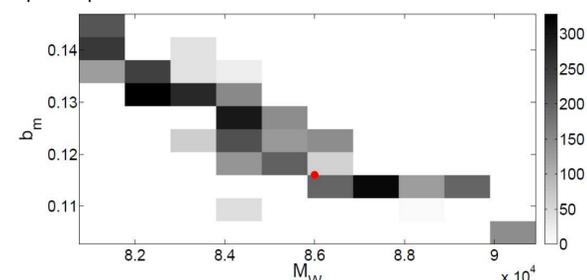


Figure 3: Weight-averaged M_w and average number of branches on a single molecule, b_m distributions for HDB 3 sampled by the MCMC algorithm.

-LVE + M

- Experimentally determined M_w is incorporated into prior probability

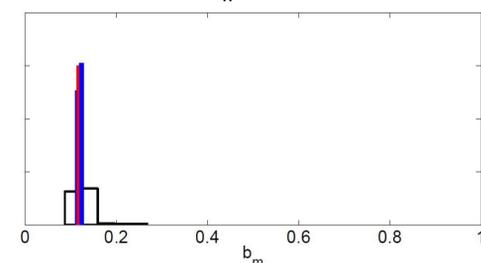


Figure 4: Weight-averaged M_w and average number of branches on a single molecule, b_m distributions for HDB 3 sampled by the MCMC algorithm.

References

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