

Determination of structural information of metallocene-catalyzed polyethylenes from Rheological measurements using a Bayesian formulation

Arsia Takeh, Sachin Shanbhag

Department of Scientific Computing, Florida State University, Tallahassee, FL



INTRODUCTION

When trace amounts of long-chain branching (LCB) is introduced into the backbone of a linear polyethylene molecule, dramatic changes in the linear and nonlinear rheology are observed. These well-documented effects include a departure from the “3.4 power law” relating the zero shear viscosity η_0 to the weight-averaged molecular weight M_w , unusually large sensitivity of η_0 to temperature or higher flow activation energies, enhanced shear thinning and strain hardening that lead to improved processibility, etc. In polyethylenes, branching in one form or another, has existed since a long time. However, recent developments in single-site metallocene catalyst technology have bestowed us with an extraordinary degree of control on molecular structure, at an industrial-scale. Notwithstanding advances in synthesis, characterization of lightly branched polyethylenes has lagged behind. It has thus become imperative to develop analytical methods that enable us to accurately detect and quantify these trace levels of LCB.

MODEL AND METHOD

Seven sets of metallocene-catalyzed polyethylenes from Wood-Adams et al. are considered in this paper. They range between one branch point every 15 molecules (HDB1), to one branch point every other molecule (HDB7).

We digitized the LVE data from published figures.

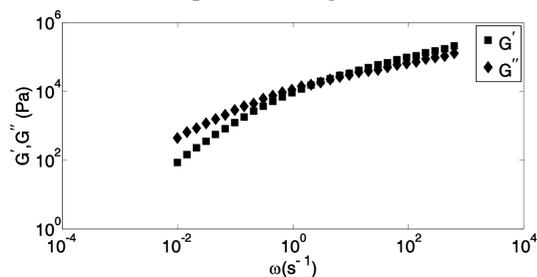


Fig1: Experimental LVE data for HDB7, showing storage (squares) and loss (diamonds) moduli. For clarity, only every fifth data point is plotted.

Seven sets of metallocene-catalyzed polyethylenes from Wood-Adams et al. are considered in this paper. They range between one branch point every 15 molecules (HDB1), to one branch point every other molecule (HDB7). We digitized the LVE data from published figures.

Wood-Adams et al. reported the experimentally measured overall GPC. To test the suitability of the Read-McLeish algorithm in describing the experimental samples, we used the nominal M_w and b_m reported in Das et al., and to generate the ensemble of branched structures. The simulated and experimental GPC curves for all the samples, are in excellent agreement.

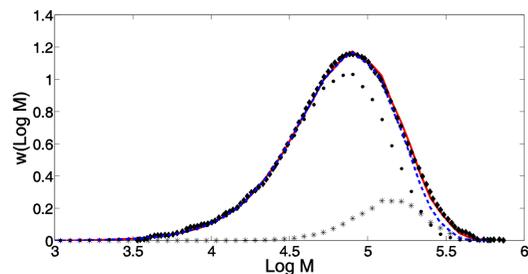


Fig2: GPC curves for HDB1. Black diamonds and red lines, respectively, are experimental GPC from Wood-Adams et al. and GPC data from BoB.

As our forward model we used the branch-on-branch model (BoB) of Das et al.. It is a general algorithm based on the tube model and hierarchical relaxation, capable of predicting the linear rheology of arbitrary mixtures of polymers of arbitrary architectures. For mPE, BoB accepts two-parameter inputs of the type, $\theta = \{M_w, b_m\}$ which is a two-state vector. It produces the corresponding ensemble of molecules. Once the ensemble is generated, it predicts the linear rheology using a time-stepping algorithm to obtain the decay of the time dependent modulus. The corresponding Fourier transforms $G'(\omega)$ and $G''(\omega)$ are denoted by $m(\theta)$.

Error between the model prediction and experimental data:

$$\varepsilon(\bar{\theta}) = \frac{1}{2} \sum (\log \frac{G'(\omega)}{G'_{\text{exp}}(\omega)}) + \frac{1}{2} \sum (\log \frac{G''(\omega)}{G''_{\text{exp}}(\omega)})$$

A likelihood function which penalizes the error between the experimental and predicted dynamic moduli is formulated as:

$$\pi(d | \bar{\theta}) = e^{-\alpha \varepsilon(\bar{\theta})}$$

we consider two scenarios (and perform two types of simulations), depending upon the availability of molecular-weight information. The two scenarios are motivated by considering potential practical applications of analytical rheology of mPEs. It is conceivable that only LVE data (which is easier to measure) on an unknown sample is available, and a quick initial estimate of the M_w and b_m is required. This corresponds to the first scenario, which we label as the “LVE” scenario. However, it is quite routine in industrial practice to run samples through SEC or GPC columns, and often this data is available in addition to LVE. This corresponds to the second scenario, which we label as the “LVE+M” scenario, where the experimentally measured M_w , M_w^{exp} , is known. Depending on the scenario, we define a so-called prior probability which summarizes our a priori knowledge of the system parameters.

For either scenario, the posterior probability modifies the corresponding prior probability based on Bayes theorem,

$$\pi(\bar{\theta} | d) = \frac{\pi(d | \bar{\theta})\pi(\bar{\theta})}{\sum_{\bar{\theta}} \pi(d | \bar{\theta})\pi(\bar{\theta})}$$

The denominator is a sum over all possible structures. We seek to sample to determine the set of structures, $\bar{\theta}$, consistent with the data d , via the above equation using a MCMC formulation.

RESULTS

LVE Scenario

In the absence of molecular weight information, the Markov chain samples two parameters (M_w and b_m). We split the simulation into 20 independent runs of 400 MCS. On average, an MCS took about 4-6 minutes (depending on M_w and b_m) on a single modern processor.

The results are generally in good agreement with the values experimentally determined by GPC and NMR, indicated by the red dots on the charts. This claim is made in light of fact that the range of the axes are quite narrow, and that there are errors inherent in these standard analytical techniques themselves.

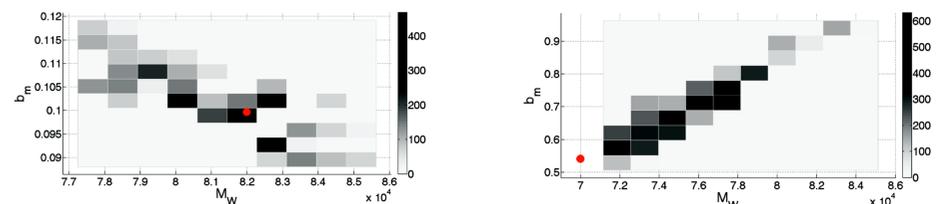


Fig3: Weight-averaged M_w , and average number of branches on a single molecule, b_m distributions for HDB2 and HDB7, sampled by the MCMC algorithm. Dark regions correspond to histogram peaks, and the red dot denotes the experimentally determined nominal values of M_w and b_m .

LVE+M Scenario

When M_w^{exp} is available and incorporated into the prior probability, the Markov chains sample only one parameter b_m . Therefore, the number of MCS required for adequate sampling is considerably smaller. In this study, we considered 300 MCS for each resin. Once again, the histograms are in good agreement with the experimental data. Marginal distributions of b_m computed from the joint-probability distributions reported for the LVE scenario simulations above, are also presented (empty bars), for comparison.

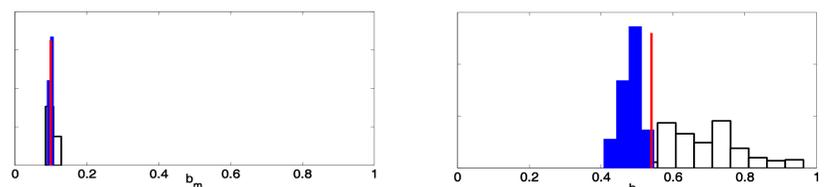


Fig4: The distribution of b_m for HDB2 and HDB7. Experimentally determined values are indicated by the red lines, marginal distribution of b_m from the LVE scenario simulations are indicated by the unfilled bars, and values from the LVE+M scenario are indicated by the blue filled bars.

REFERENCES

- Wood-Adams et al., Macromolecules 2000, 33, 7489-7499
Das et al., Journal of Rheology 2006, 50, 207-239