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The Influence of Branching Architecture on Scission in Modeling Free-Radical Polymerization with Long Chain Branching and Scission

Piet D. Iedema* and Huub C. J. Hoefsloot

Abstract: In modeling molecular weight (MWD) and degree of branching (DBD) distribution for radical polymerization systems, assumptions have to be made concerning the length and the number of branches of fragments from scission reactions. The linear-chain approximation with respect to scission kinetics usually applied is shown to be incorrect. A new method is proposed based on a mechanistic model predicting architectures. It is shown that a simple short/long chain fragment scission assumption significantly changes the predicted MWD.

Keywords: Degree of branching distribution · Long chain branching · Low-density polyethylene · Molecular weight distribution · Scission

Introduction

In models predicting the molecular weight and degree of branching distribution of radical polymerization with long chain branching and scission, the assumptions concerning length and number of branches on fragments are crucial. Here, we focus on the impact of *branching architectures* on scission. Until now, the linear-chain approximation has been employed, which describes the scission of linear chains with branch points (Iedema *et al.* [1], Hutchinson [2]). This article shows, however, that this assumption does not describe scission kinetics of branched molecules correctly. It is proposed that architecture-based scission kinetics, based on our architectures synthesis algorithm, be implemented in the model predicting MWD/DBD. The results of a full implementation are not yet available, but the effect of non-linear scission *i.e.* a preference for short and long chains – on the MWD has been explored. Quite remarkably, the generally observed bimodality in the MWD vanishes with preferred short/long scission.

Here, first the MWD/DBD model is presented, including the most important assumptions being made. Then some examples of the effect of branches on scission statistics are given. Our branched architectures synthesis is briefly described. Finally, the impact of short/long scission is presented and discussed.

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Molecular Weight Distribution (MWD) and Degree of Branching Distribution (DBD)

In the reaction scheme branching and scission are given by Eqn 1 and 2.

$$R_n^{\,i} + P_m^{\,j} \xrightarrow{k_{tp}m} P_n^{\,i} + R_m^{\,j+1} \quad (1)$$

$$R_n^{\,i} + P_m^{\,j} \xrightarrow{k_{rs}m} P_n^{\,i} + R_{m-l}^{\beta(m,j,m-l,j-k)} + P_l^{\beta(m,j,l,k)} \quad (2)$$

The complexity of scission in Eqn (2) is expressed in the upper case index of the chain fragments, β. This denotes the number of branches, which in principle is a function of the length and number of branches of the original chain, m and j, respectively, and the length and number of branches on the chain fragments, m-l and j-k. When computing the MWD only, as a first approximation the balance of the branches is not taken into account, yielding distributions like the one in Fig. 1. Notice that here scission of a chain of length n into fragments of n-r and r is equally probable for each r.

In order to find the DBD, we solved the branching balance using pseudo distributions (Iedema *et al.* [1]) like the one defined as the first moment distribution for the dead chains:

$$\Psi_n = \sum_{i=0}^{\infty} i P_n^i$$

In our first approach the problem to find the number of branches on fragments was resolved by assuming that fragment length and number of branches on them were completely independent. Later, Hutchinson [2], using a hypergeometric distribution has improved this. The chemical concept can be viewed as breaking linear chains with branch points, branch lengths themselves being zero. Thus, we find a DBD as in Fig. 2. Note that since the assumption regarding numbers of branches on fragments only appears in the balance equations for the pseudo-distributions, it only affects the DBD and does not change the (bimodal) MWD.

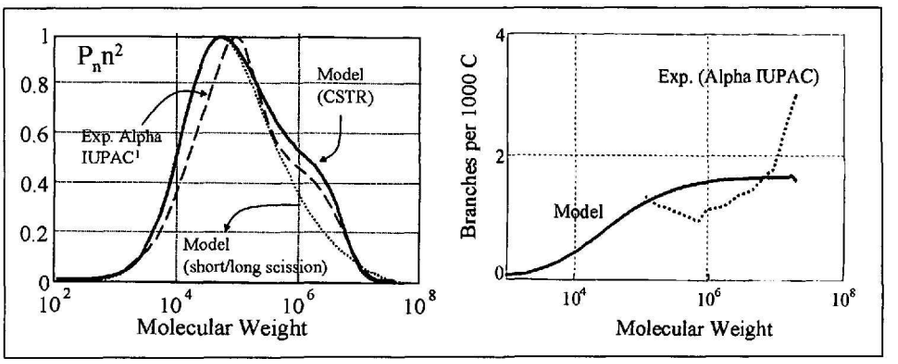

Fig. 1. Molecular weight (left) and degree of branching (right) distribution for autoclave ldPE as predicted by the model and measured by size exclusion chromatography (SEC). Broken line in the figure left from model, assuming simple long/short fragment scission.

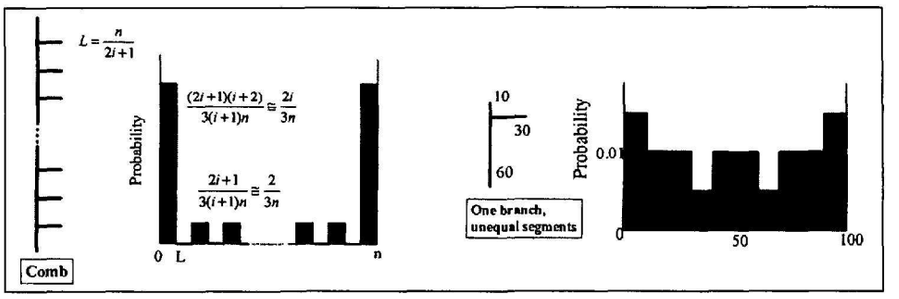

Fig. 2. Fragment length distribution from scission of comb structures of length n with i branches and equal segment lengths L (left) and from scission of single-branched polymer of length 100 and unequal segment lengths.

Influence of Architecture on Scission

Obviously, the linear chain approximation is a simplification, since branched architectures will break differently. This is demonstrated by a few examples of breaking combs and Cayley trees with equal and unequal segment lengths (Fig. 3).

Thus, we see that scission of chains with length n into fragments of n-r and r depends on the position of r in the architecture. Scission is more likely to produce long and short fragments than fragments of equal lengths. Also, these short fragments are mostly non-branched. Clearly, fragmentation proceeds differently for combs or Cayley trees. This proves that accounting for architectures is highly desired.

Architecture Modeling

We have developed an architecture synthesis algorithm, which employs the concept of 'primary polymers' as building blocks and based on graph theory and Monte Carlo sampling (Iedema and Hoefsloot [3]). Thus, individual molecules (Fig. 3) could be rapidly synthesized from MWD/DBD with as much detail as full Monte Carlo methods. The explicit knowledge of architectures provides all information needed to describe fragmentation correctly. The interesting idea now is to utilize this architectural information and translate it to scission kinetics in the model calculating MWD and DBD. Note that in this approach scission kinetics are treated differently with respect to both length of the fragments and the number of branches on them. Hence, it is expected that not only DBD but also MWD predictions by the model will change. A model is presently under construction that integrates the architectural features into the Galerkin kinetic model. In order to explore the effects of architecture-based scission kinetics on MWD/DBD, we performed a number of calculations exercises using a strongly simplified approach of such kinetics, as will be shown in the next section.

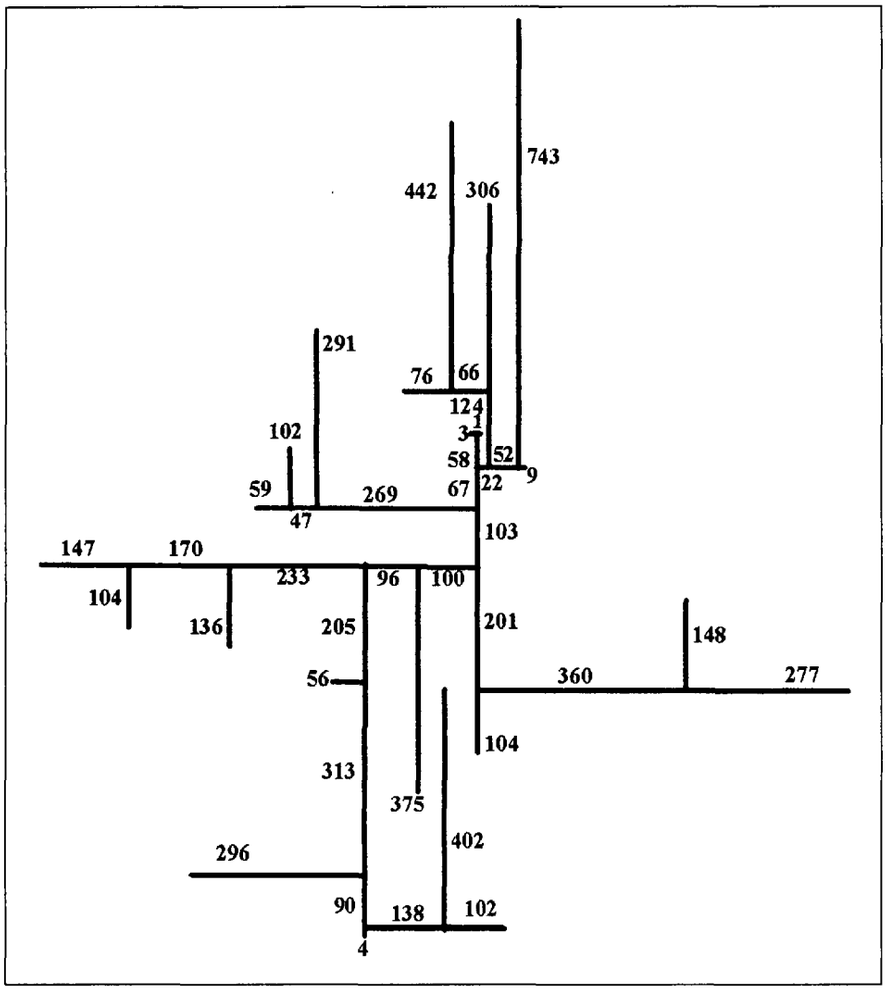

Fig. 3. Architecture of ldPE molecule according to bivariate MWD/DBD distribution (Fig. 1 and 2) with length n = 6897 and 20 branch points.

Scission into Long and Short Fragments

From the simple examples presented above it turns out that architecture scission tends to yield longer and shorter fragments rather than fragments of equal length. In order to obtain an idea of the direction of change in the MWD shape we investigated a simple case of unequal scission. The maximum length of the small fragment is assumed to be around the average segment length of 400 monomer units by multiplying the rate coefficient by a probability function f(m) = 400/(400+m), where m is the length of the smallest fragment. Implementing this in the Galerkin model led to some interesting results. Considerable weakening of the scission results in a and broadening of the MWD. Fig. 1 quite remarkably shows that the bimodality completely vanishes in this case of simple short/long scission. Obviously, the real situation is far more complex and should be described by an integrated MWD/DBD predicting model accounting for architecture-based scission kinetics. However, on the basis of these first results we are inclined to expect that the introduction of architecture-based scission will suppress the bimodality.

Conclusion

Modeling the molecular weight and degree of branching distribution of ldPE in a CSTR requires an assumption about the number of branches on the fragments of the scission reaction. Until now the problem has been solved by employing the concept of linear chains with branch points (Iedema *et al.* [1], Hutchinson [2]). Variations within this concept only affect the DBD, while the typical bimodal shape of the MWD remains unchanged. However, with some simple examples it is shown that chains with branched architectures really have different scission kinetics than linear chains. We propose to replace the linear-chain approximation by integrating our model predicting architectures from the MWD/DBD in the kinetic model that predicts these distributions. Since this implies a really different description of the scission kinetics, we expect the predicted MWD and DBD both to change. This has been confirmed by a simple approach of non-linear chain breaking scission, in fact describing the preference of breaking into short and long fragments. Doing so it has been shown that the bimodality of the MWD completely vanishes. Obviously, a full implementation of architecture dependence is required to a definitive conclusion on this issue.

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