Branching determination from radius of gyration contraction factor in radical polymerization

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ABSTRACT

This paper proposes a set of models to calculate contraction factor, which to maximum extent accounts for the kinetics of radical polymerization with transfer to polymer and recombination termination. The models are alternatives to the Zimm and Stockmayer's (1949) analytical expression of contraction factor for molecules with terminal branching. The results, being representative for polymers like as low-density Polyethylene (ldPE), show significantly stronger contraction than predicted by the model of Zimm and Stockmayer. In the case of termination by disproportionation only, molecular sizes turn out to be smaller by a factor of almost two. In presence of recombination termination molecules are less compact. It is shown that the interpretation of contraction factors as measured by the Size Exclusion − Multi-Angle Light Scattering to find the branchedness of ldPE, with the new model would lead to a considerably *lower* estimate of branching than by using Zimm and Stockmayer's model.

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1. Introduction

Zimm and Stockmayer's [1] model of branching was one of the first aiming at relating the size of a branched polymer molecule to its molecular weight. In this article we revisit their theory and extend it to account for the influence of chemical mechanisms on branching topology. Many authors after Zimm and Stockmeyer have since considered the size−molecular weight relationship, either from a chemical or from physical viewpoint. To the first group of studies belong those devoted to the structure of branched polymers *being* created during polymerization [2−13] − as is the case with the present paper. The second group has studied size of branched polymer molecules *after* being created and focus on physical and thermodynamic issues arising from excluded volume effects and the environment of the molecules − present in solutions or melts. In their study Zimm & Stockmeyer had to completely ignore such issues. In the polymer physics area models of branched polymers have been developed based on universal scaling laws by De Gennes [Burchard, [14]], allowing for inhibited interpenetration typical for branched polymers. Another is the elegant 'Random Branching Theory (RBT)' [Konkolewicz et al., [15−17]], and its application to laboratory synthesized branched polymers, which describes branched polymers using mass density distributions and thus is able to include effects like inter-segmental repulsion. Interestingly, one of these studies [Konkolewicz et al., [17]], introduces kinetics into RBT (KRBT) allowing finding model parameters employing MWD-data. Although different parameters are found for different chemical systems, no direct link exists between these and chemical rate coefficients. Most studies in the chemical area, like the present one, are indeed based on chemical rate coefficients. A further difference of chemical models with KRBT is explicit accounting for topology with monomeric resolution, whereas (K)RBT adopts more coarse grained units. Most chemical models, on the other hand, do not account for excluded volume or repulsion effects. As regards contraction factor, when comparing linear and branched molecules under the same conditions, such effects will cancel out to a certain extent. Apart from being important with respect to molecular size, model descriptions on the level of explicit branching topology with monomeric resolution also provide crucial information in predicting viscous-elastic behavior. For low-density Polyethylene (ldPE), the branched structure in relation to rheology and melt strength has been discussed recently in Science [18].

A number of techniques are available to determine branching of polymers: multi-detector size exclusion chromatography (SEC), ^{13}C

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NMR and IR-spectrometry. With respect to SEC the Zimm & Stockmeyer theory has been widely used to quantify branching, where the key factor is the higher compactness of branched polymer molecules compared to their linear counterparts, expressed as the 'contraction factor'. SEC and ^{13}C NMR have been applied to crosslinking polymerization of mixes of mono- and di-acrylates [Gaborieau et al., [19,20]]. For poly-olefins with both short (SCB) and long branches (LCB), caused by different chemical mechanisms as in ldPE, the use of ^{13}C NMR is more complicated. At present, with ^{13}C NMR one may distinguish between side chains of up till 6 C atoms, but longer side chains are indistinguishable. In those cases SEC combined with multi-angle light scattering (MALS) seems to be preferable to quantify LCB [21–25]. After Ref. [21] the ratio of intrinsic viscosities of branched and linear polymer fractions eluting at the same time in SEC − closely related to contraction factor − are calculated using the average molar mass of branched polymer from MALS. In all of these studies of branching, mostly in ldPE, SEC-MALS has been employed and the old Zimm & Stockmeyer model has been used to quantify LCB on the basis of contraction factor data.

Examples of modeling studies accounting for branching are [26,27], which present numerical fractionation techniques and the method of moments applied to each class of branched molecules to compute the molecular weight and degree of branching, where branching is caused by chain transfer to polymer. Further, predictions of the degree of branching distribution (DBD) and molecular weight distribution (MWD) accounting for random scission, and thereby generating the exact architectures of the branched molecules by applying Monte Carlo (MC) simulations is provided in Refs. [2–5] by Tobita. From this information, the mean square radius of gyration could be obtained by explicitly constructing the conformations of the branched molecules. Instead in Ref. [6], we used a statistical mechanical theory on the basis of a graph theoretical representation of branched molecules to find the radius of gyration has. This was the first study showing that the Zimm & Stockmeyer theory under-estimates the contraction of branched polymers as compared to topologies predicted allowing for a realistic branching process, transfer to polymer in that case. Later, this has been confirmed using Monte Carlo simulation [13,28]. In Ref. [29], the contraction factor for stars with arms with a Flory [30] distribution is calculated and it is shown that the contraction factor distribution for this type of star molecules is the same as for stars with uniformly distributed arms.

The question we desire to answer in this paper is essentially the same as Zimm and Stockmayer's in 1949 [1]: how could we relate long chain branching to radius of gyration contraction factors? This has obvious practical relevance in characterization of branched polymers by SEC-MALS, since up until today the theory of Zimm and Stockmayer is used to estimate branching from the observed contraction factor. We will call to mind that Zimm and Stockmayer just claimed the validity of their model for a simple end-to-end branching structure. After more than 60 years with powerful computers and good mathematical models we are now able to predict branched architectures based on the real polymerization kinetics. Using the same concepts as Zimm and Stockmayer, we will demonstrate that these more realistic architectures give rise to different contraction factors than those from the old model. This will be exemplified by a radical polymerization system resembling ldPE with transfer to polymer as the branching mechanism and recombination termination. The latter mechanism introduces an extra connectivity element, since parts of a molecule are not only connected by branch points, but also by combination points. It will be shown that absence or presence of recombination termination is strongly influencing the compactness of the molecules. Although our new model is demonstrated

on branched ldPE, its principles are readily applicable to other branched polymers. Indeed, it would form an interesting method to predict topologies for a whole new class of hyperbranched polymers synthesized with the 'Strathclyde' approach [31,32] using acrylates, Self-Condensing Vinyl Polymerization (SCVP), Reversible Addition-Fragmentation chain Transfer (RAFT) polymerization and Atom Transfer Radical Polymerization (ATRP).

The paper will start briefly resuming Zimm and Stockmayer's concept of finding the radius of gyration from a branched polymer structure. A procedure is presented, consisting of several steps to find the explicit architectures and their contraction factors. As the first steps, the definition of the polymerization reactions assumed is given, and a model to predict the 3-dimensional (3D) distribution of chain length, number of branch points and number of combination points is proposed. Then, the growth history backtracking algorithm is described, which provides populations of explicit branched architectures based on a conditional Monte Carlo simulation method. Subsequently, a method to calculate the radius of gyration contraction factor, using graph theory to describe the architectures, is given. This completes the procedure to find contraction factors. Results are then presented, comparing our outcomes to those based on the Zimm and Stockmayer theory. Finally, a hypothetical case of reversely interpreting a given contraction factor to infer branching from, is discussed.

2. Zimm and Stockmayer revisited

Here, we briefly discuss the paper by Zimm and Stockmayer [1] that provided the classical estimation of branching by using the radius of gyration. According to the usual definition (see Fig. 1), the radius of gyration is defined as the sum of the distances between each monomer unit, r_k, and the center of mass, $\bar{r}$. For highly branched molecules they adopt Kramers theorem [33], using a 'segment' length b, whch is the reference size of a monomer unit in the polymer chain:
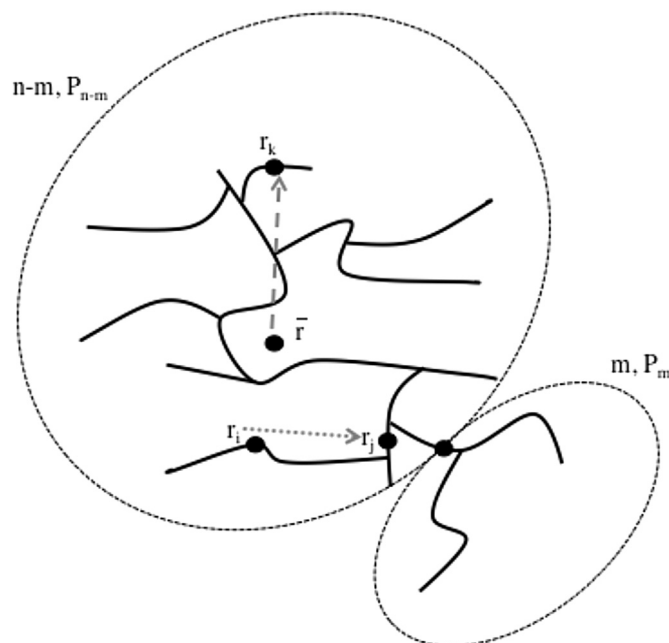

Fig. 1. Radius of gyration from distances to center of mass and from products of distances between monomer units.