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On the contraction factors of long-chain branched macromolecules

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ABSTRACT

For several decades, the relation between the contraction factor of radius of gyration for branched macromolecules, g , and that of intrinsic viscosity, g' , has been presented as $g' = g^{\epsilon}$. The value of ϵ was assumed to be constant for branched macromolecules of a certain type, such as stars, or combs, or statistically branched macromolecules. Experimentally determined values of ϵ , however, turn out in the majority of cases to be molecular-weight dependent. The present study shows that molecular-weight-independent values of ϵ can be expected only for a plurality of molecules with identical architecture. By branched molecules with identical architecture we mean molecules in which with varying degree of polymerization the ratios of the degrees of polymerization of all sub-chains remain constant, irrespective of the integral degree of polymerization of individual molecules. Also, it has been demonstrated that the ratio of intrinsic viscosities of a linear and a branched polymer molecule having the same hydrodynamic volume, $[\eta]_{l,v}/[\eta]_{b,v} < 1$, is a measure of the relative increase of the volume fraction of polymer segments within the domain of a macromolecule due to branching.

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1. Introduction

In the characterization of branched polymers with long-chain branching (LCB), one of the essential parameters is the degree of branching. Most frequently, the concentration of branch points in polymer molecules is much too low to be amenable to acceptably accurate direct determination by, e.g. nuclear magnetic resonance. Then, one has to resort to methods utilizing the fact that the volume of the domain occupied by a branched macromolecule in solution is always smaller than the volume of the domain occupied by a linear macromolecule of the same polymer with the same molecular weight, because the branched molecules are more densely packed. Nowadays, the most convenient experimental technique for the characterization of LCB polymers is size-exclusion chromatography (SEC) with concentration, light-scattering and viscosity

detection. The combination of the signals of the two first-mentioned detectors enables us to determine the molecular weight, M , of the SEC slices and the combination of the signals of the concentration and viscosity detectors is instrumental for the calculation of the value of the intrinsic viscosity of the SEC slices.

If the intensity of light scattered by a dilute polymer solution, expressed as the Rayleigh ratio, depends on the angle of observation, i.e. the polymer molecules are larger than approximately 1/10 of the wavelength of the incident light, one can determine the radius of gyration of the dissolved macromolecules, an important size parameter [1]. The radius-of-gyration contraction factor, g , a measure of the degree of branching, is defined as the ratio of the mean-square average radius of gyration of a branched macromolecule, $\langle s^2 \rangle_{bM}$, and the mean-square average radius of gyration of a chemically identical linear macromolecule with the same molecular weight, $\langle s^2 \rangle_{lM}$:

$$g = \langle s^2 \rangle_{bM} / \langle s^2 \rangle_{lM} \quad (1)$$

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Its value decreases with increasing degree of branching.

Another characteristic of the degree of branching is the intrinsic-viscosity contraction factor, g' , defined as the ratio of intrinsic viscosities of a branched molecule, $[\eta]_{\text{bM}}$, and a chemically identical linear molecule, $[\eta]_{\text{lM}}$, with the same molecular weight:

$$g' = [\eta]_{\text{bM}} / [\eta]_{\text{lM}} \quad (2)$$

The value of g' decreases with increasing degree of branching as well.

Let us observe that also other terms, such as branching index, shrinking [2] or shrinkage [3] factor and geometric parameter [4] have been used for the contraction factors in the literature.

In the last two decades, attention was paid to the contraction factors of various types of polymers with long-chain branching: stars [5–9], combs [7,10], regular combs and centipedes [3], polymers with tri-functional branch points [11–13], among them low-density polyethylene because of its immense importance in everyday life [14–16], polymers with two branch points in a molecule [7], e.g. H-shaped polybutadienes [17], polymers synthesized using a tetra-functional initiator [18], hyperbranched polysaccharides [2], copolymers of vinyl and divinyl monomers [4,19–23], polymers prepared by cross-linking of linear polymers [24], and dendrimer-like and hyperbranched polymers [25]. Many more relevant references can be found in recent reviews [26,27].

Each of the two contraction factors, g and g' , has its advantages and drawbacks. The radius-of-gyration contraction factor, g , can be measured with plausible accuracy only for macromolecules with a relatively high molecular weight, typically with $M > 1 \times 10^5$, whereas the intrinsic-viscosity contraction factor, g' , can be determined with fair accuracy in a practically unlimited range of molecular weights. On the other hand, the radius of gyration can, in principle and under certain assumptions, be calculated from the constitution of a macromolecule, whereas the theory of intrinsic viscosity is not mature enough to predict its value for complex structures of branched macromolecules [28]. This suggests that it is desirable to have a tool for converting g into g' and vice versa.

The relation between g and g' has been formulated repeatedly as:

$$g' = g^\varepsilon \quad (3)$$

where the exponent ε depends on the type of branching and theoretically varies over a wide range of 0.5 for star-like and 1.5 for comb-like macromolecules [29]. References to particular exponent values experimentally determined for specific branched polymers can be found in Shiga's review [30]. Many authors expect constant values for the above exponents for all star-like or comb-like or other types of branched molecules. Repeatedly, questions have been asked such as: "It was of special interest whether a relation between g and g' could be found, that remains universally valid for all types of branched polymers." [31] or "...but there is still much debate about the value of ε for different branched architectures and whether the parameter is universal for all branched polymers" [3].

Those questions may be ill posed. An irregular star, i.e. a star with arms of different lengths, approaches with increasing diversity in arm lengths the topology of a linear molecule if the lengths of two arms predominate. So does a comb-like molecule with a long backbone and short side-chains. And indeed, it has been observed that the intrinsic viscosities of the combs are close to the intrinsic viscosities of the parent backbone polymer itself [3]. On the other hand, a comb-like molecule with a short backbone and long side-chains or grafts is, in the limit, a star molecule.

In statistically branched polymers with any branch-point functionality, in any SEC slice, a broad spectrum of molecules with the same hydrodynamic volume is present, the individual molecules differing in molecular weight, number of branch points per molecule, and molecular architecture. The ratios of the mass fractions of individual species vary with the elution volume. For this type of polymers, hardly any generally valid value of the exponent ε can be expected. An increase in the value of the exponent ε from about 0.5 to 1.3 with increasing molecular weight has been observed for statistically branched polymers (Fig. 13 in Ref. [12]) and interpreted as a change in the branching architecture from star-like to comb-like. This shows that a rigorous conversion of g' to g using Eq. (3) is not universally feasible and the value of g' gains importance.

We speculate that the exponent ε is constant and independent of molecular weight only for a plurality of molecules with identical architecture. In the following, we are going to scrutinize this hypothesis. By branched molecules with identical architecture we mean molecules in which with varying degree of polymerization the ratios of the degrees of polymerization of all sub-chains remain constant, irrespective of the integral degree of polymerization of individual molecules (Fig. 1).

2. Theory

2.1. Contraction factors and molecular architecture

The generally accepted relation $g' = g^\varepsilon$ (Eq. (3)) presumes that ε is a constant for a given type of branching and architecture and the contraction factors g and g' are independent of molecular weight. However, most reaction mechanisms leading to branched polymers of various types result in polymers in which the molecular architecture varies and the degree of branching increases with

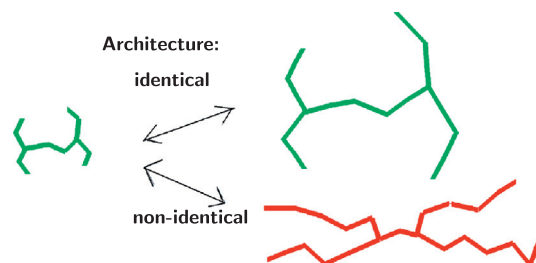


Fig. 1. Scheme of long-chain branched molecules with identical and non-identical architectures.

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