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Characterization of branched polymers

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SUMMARY: Most long-chain-branched polymers occurring in practice are formed by processes statistical in nature and this results in substances highly non-uniform in molecular weight, number of branch points per molecule, and in the architecture of molecules with a particular number of branch points. The most reliable information on the degree of branching is obtained by determining the weight-average molecular weight, by light scattering, and the intrinsic viscosity, and by comparing the intrinsic viscosity with that of a linear polymer with the same weight-average molecular weight. If an appropriate model exists for the particular polymer, its more detailed description may be possible.

Introduction

Branching and cross-linking of macromolecules affect the properties of polymer materials. Thus, it is important to characterize the structure of branched polymers on the molecular level. Short-chain branches can be identified by spectroscopic techniques, NMR in particular. The problem is more complex with long-chain branching. It is relatively easy to prove the presence of long-chain branching qualitatively, but a quantitative description is a much harder task.

For academic studies, branched polymers with defined architecture can be tailored$^{1)}$. With these substances, the molecular parameters, such as molecular weight, radius of gyration, hydrodynamic volume and intrinsic viscosity, usually have the values predicted on the basis of the process of synthesis and an appropriate theoretical model.

Most branched polymers occurring in practice are formed by processes statistical in nature and this results in substances comprising macromolecules highly non-uniform in molecular weight, number of branch points in a molecule, and in the architecture of molecules with a particular value of molecular weight and number of branch points. Rigorous quantitative description of such polymers in terms of molecular parameters is extremely difficult and often unfeasible.

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This communication qualitatively reviews the features of the molecular structure of polymers with statistically generated long-chain branching and the potentials and limitations of experimental techniques presently available for their characterization on the molecular level.

Molecular-weight distribution

Most of the contemporary models of molecular-weight distributions (MWDs) are still, after more than fifty years, based on the classical papers by W.H. Stockmayer[2,3]. The MWDs of statistically branched polymers prior to the gel point or of their soluble fractions, the sol, beyond the gel point have a number of characteristic features (Fig. 1):

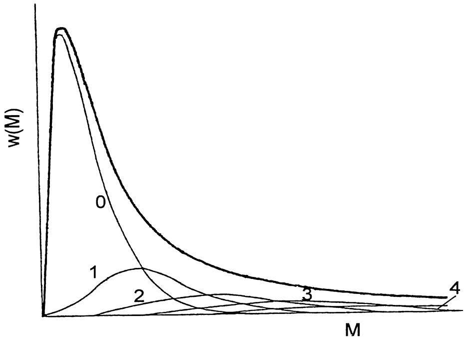

Fig. 1: Sketch of a differential mass distribution function, w(M), of a statistically branched polymer close to the gel point. The thick line is the overall distribution function. Thin lines are the distribution functions of macromolecules with zero, one, two, three, etc, branch points per molecule

1. They can be looked on as a superposition of partial distributions of linear macromolecules and macromolecules with one, two, three, etc, branch points.
2. Branching always leads to broadening of MWD in comparison with the distribution which would result under otherwise identical conditions in the absence of branching.

3. Even in the proximity of the gel point, the polymer contains a substantial mass fraction of linear, non-branched macromolecules.
4. The average molecular weight of a fraction of macromolecules with a definite number of branch points increases with the number of branch points.
5. The presence of high-molecular-weight branched macromolecules gives rise to a high molecular-weight tail of the MWD, resulting in its broadening.

Fractionation

In order to determine the MWD, the polymer has to be fractionated with respect to molecular weight. With branched polymers, the separation process of any type is affected not only by molecular weight but also by the degree of branching and architecture of the macromolecules. For fractionation, two types of methods are currently being used, namely, size-exclusion chromatography (SEC) and phase separation in dilute solutions.

For analytical purposes, SEC is of course the method of choice. SEC separates the macromolecules according to hydrodynamic volume rather than molecular weight. Because of more compact structure, branched molecules always have a smaller hydrodynamic volume than linear molecules with the same molecular weight. Consequently, a SEC fraction may be reasonably uniform with respect to hydrodynamic volume but still comprise a broad spectrum of macromolecules with various combinations of molecular weights, number of branch points and architecture of the molecule. The width of this local non-uniformity4) increases with the degree of branching and may be quite broad for the highly branched, high-molecular-weight fractions.

To get an idea of the importance of molecular architecture, the simplest case of a macromolecule with one tri-functional branch point is mentioned. If the branch point is located close to one of the three chain ends, the size of the molecule and its hydrodynamic volume do not differ too much from those parameters of a linear macromolecule with the same molecular weight. On the other hand, if the branch point is placed in equal distance from all the three chain ends, the molecule assumes the shape of a regular three-arm star and its size parameters are considerably smaller than those of a linear macromolecule with the same molecular weight.

For preparative purposes, fractionation based on phase separation in dilute solutions is used in the mode of either precipitation or extraction fractionation. The precipitation fractionation seems to yield better results. As a rule, branched macromolecules precipitate earlier than linear molecules with the same molecular weight. Here again, a fraction is a mixture of a wide variety of molecular species differing in molecular weight, degree of branching and molecular architecture. A fraction comprises macromolecules with compact branched structures and lower molecular weights together with less branched, less compact macromolecules with higher molecular weights, and linear macromolecules with the highest molecular weight. The fractions obtained by precipitation fractionation are always rather non-uniform with respect to molecular weight, particularly so the high-molecular-weight fractions, which are strongly branched (Fig. 1).

At the present time, no method is available which would enable us to separate branched macromolecules purely according to molecular weight. Consequently, the experimental determination of MWD of long-chain-branched polymers is always charged with an error increasing with the degree of branching.

Light scattering

Static light scattering, small-angle x-ray scattering, and small-angle neutron scattering give information on the size and shape of macromolecules and could, in principle, be used for the characterization of the degree of branching. The most widely used technique is, for a number of reasons, light scattering[5)] and the following discussion will focus on this method. After all, due to the common physical basis of the three techniques, the argument applies with appropriate modification to all of them.

From conventional light-scattering measurements with dilute polymer solutions, the following information can be obtained:

1. Molecular weight, M, for uniform polymers and the weight-average molecular weight, M_w, for non-uniform polymers.
2. Radius of gyration, R_G, for uniform polymers and the z-average radius of gyration, $R_{G,z}$, for non-uniform polymers, provided the macromolecules are larger than some 20–30 nm. This corresponds typically to molecular weights 1×10^5 – 2×10^5. Only then, the angular

dependence of the intensity of scattered light is large enough to permit a tolerably accurate determination of the radius of gyration.

3. For very large macromolecules, typically with molecular weights of a few millions, some conclusions on the shape of macromolecules, eg, on the degree of branching, may be drawn from the angular dependence of the intensity of scattered light. But it is to be emphasized that the macromolecules must be strictly uniform with respect to molecular weight and structure, otherwise fallacious conclusions might be made. The reason is that the angular dependence of the intensity of scattered light is affected equally strongly by the shape of the macromolecules and their non-uniformity in molecular weight, and there is virtually no reliable way of separating these two effects from each other. Unless the polymer is a carefully prepared model substance with well defined structure, it is not advisable to try to make any conclusions regarding the shape of the macromolecules, eg, the degree of branching, from the angular dependence of the scattering intensity.

A long-chain branched macromolecule is more compact and, therefore, has a smaller radius of gyration than a linear macromolecule with the same molecular weight. For various models of branched macromolecules, the reduction in R_G due to branching has been calculated6). For uniform branched polymers, the ratio of the radii of gyration of a branched, $R_{G,b}$, and a linear, $R_{G,l}$, macromolecule with the same molecular weight enables us, in principle, to determine the degree of branching. Unfortunately, this situation does not occur in practice very often.

The problem is much more complex with non-uniform branched polymers7). The source of trouble is the physical reality that light scattering yields different averages for molecular weight and radius of gyration, viz, weight-average molecular weight and the z-average radius of gyration. Due to its definition, the z-average radius of gyration is more sensitive to the high-molecular-weight portion of a non-uniform polymer than the weight-average molecular weight. In other words, the $R_{G,z}$ value obtained from a light-scattering measurement is larger than the radius of gyration corresponding to a macromolecule with molecular weight equal to M_w, and the two quantities cannot be correlated straightforwardly.

With non-fractionated, statistically branched polymers, the increasing degree of branching reduces the radii of gyration. On the other hand, with increasing degree of branching the molecular-weight distribution broadens and this enhances the discrepancy between $R_{G,z}$ and M_w. The increasing degree of branching and the concomitant broadening of MWD have opposite effects on $R_{G,z}$, this results in a far-reaching compensation of both factors obscuring the presence of branching$^{5)}$.

It is worth mentioning that the compensation of the effects of branching and non-uniformity on $R_{G,z}$ is complete or almost complete in many practically important systems. For instance, if a linear polymer with the most probable MWD is randomly cross-linked, $R_{G,z}$ varies with M_w in exactly the same way in the linear and all arising branched systems with any degree of branching. In other words, at equal M_w values, a linear polymer with the most probable MWD and all randomly branched, non-uniform polymers derived from it, with any degree of branching up to the gel point, have identical $R_{G,z}$ dependences on M_w and, hence, the comparison of the two radii of gyration, $R_{G,z,b}$ and $R_{G,z,l}$, at a particular value of M_w gives no information on branching whatsoever.

Fractionated, less non-uniform statistically branched polymers have, at equal values of M_w, smaller values of $R_{G,z,b}$ than linear polymers but the interpretation in terms of the degree of branching is still not very reliable due to the often significant residual non-uniformity of the fractions.

It should be concluded that it is an exception rather than the rule if reliable information on long-chain branching can be obtained by light scattering itself.

Intrinsic viscosity

The intrinsic viscosity is a measure of the volume occupied by a macromolecule in dilute solution. As long-chain-branched molecules have a more compact structure than the linear molecules at equal molecular weight, the intrinsic viscosity of a branched polymer is smaller than that of a linear polymer$^{8)}$. For instance, one and two tri-functional branch points in a macromolecule reduce its intrinsic viscosity approximately by a factor of 0.9 and 0.83, respectively. For one and two tetra-functional branch points in a macromolecule, the approximate values of the reduction factor are 0.8 and 0.7, respectively. Thus, the effect of branching on intrinsic viscosity is quite distinct and can be utilized for the characterization of long-chain branching.

Theories of the intrinsic viscosity of long-chain-branched macromolecules have been developed[8-10)] for a number of models, such as star-like or comb-like macromolecules, statistically branched non-uniform polymers with tri-functional or tetra-functional branch points, etc. All theories use a number of approximations. Most of the theories make simplifying assumptions on reactivities in the synthesis of polymers. In cross-linking reactions, intra-molecular cycles are formed to a large extent[11)], but the theories neglect this important effect because of its unmanageability. Highly branched and cross-linked polymers are often not well soluble and have to be analyzed in thermodynamically good solvents, in which the excluded-volume effect is operative. As there is no generally recognized theory of the excluded-volume effect for branched polymers, this factor is mostly ignored, although its influence on the intrinsic viscosity is certainly non-negligible.

When using intrinsic viscosity for the characterization of long-chain-branched polymers, as a rule, the most adequate theory is chosen to which the experimental data are fitted. In the majority of cases, not all of the assumptions of the theory are fulfilled and one should be aware that the values of the parameters characterizing branching thus obtained have just conditional validity.

Recommended procedure

The most efficient way of characterizing long-chain-branched polymers is to determine the weight-average molecular weight, by light scattering, and the intrinsic viscosity, and to compare the intrinsic viscosity of the branched polymer with that of the chemically identical linear polymer with equal weight-average molecular weight. Depending on the task and available facilities, the measurements are performed with the whole sample, ie,. without fractionation, or with fractions after separation.

In a simple measurement without fractionation, the ratio of the intrinsic viscosities of the branched and linear polymer with identical M_w is a rough estimate of the extent of branching and is quite helpful in comparing individual specimens in a series of samples of the same polymer differing in the degree of branching. If an appropriate model has been formulated for that particular type of branching, an estimate of the average degree of branching can be made.

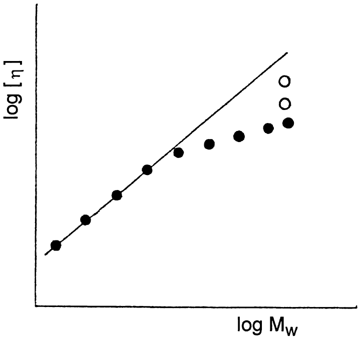

Fig. 2: Effect of branching on the molecular-weight dependence of intrinsic viscosity. The straight line is the dependence for the linear polymer. • Points for fractions of a statistically branched polymer; o points for two non-fractionated statistically branched polymers with the same weight-average molecular weight and different degrees of branching

More informative is the procedure with fractionation. Fractionation can be performed by the classical phase-separation technique7), or much more elegantly and quickly by size-exclusion chromatography12), provided the chromatograph is equipped with three detectors, viz, concentration, light-scattering, and viscosity detector13). It should be observed that in SEC analyses at both shoulders of the elution curve, the signals of all detectors are weak with respect to noise because of the high dilution. The concentrations of the highly branched fractions are very low and the values of M_w and intrinsic viscosity may be charged with a large experimental error.

Plotting the values of the intrinsic viscosity of fractions versus their M_w in logarithmic coordinates, a characteristic dependence is obtained (Fig. 2). For low molecular weights, the dependence for the branched polymer is virtually identical with that for the linear polymer because the low-molecular-weight macromolecules are predominantly linear (cf Fig. 1). With increasing molecular weight, the dependence for the branched polymer deviates more and more from the dependence for the linear polymer because the degree of branching increases with molecular weight. If the branched polymer conforms with an existing model, the degree of branching of the fractions can be determined with the qualification that the local non-uniformity of the fractions affects the results to some extent, which is difficult to assess.

Conclusion

The problem of characterization of non-uniform long-chain-branched polymers has not yet been solved satisfactorily because of the vast variety of molecular structures present in such polymers. The most reliable information is obtained by determining the weight-average molecular weight, by light scattering, and the intrinsic viscosity, and by comparing the intrinsic viscosity with that of a linear polymer with the same M_w. If an appropriate model exists, a semi-quantitative or even quantitative estimate of the degree of branching can be made.

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