# Structure and Rheology of Molten Polymers

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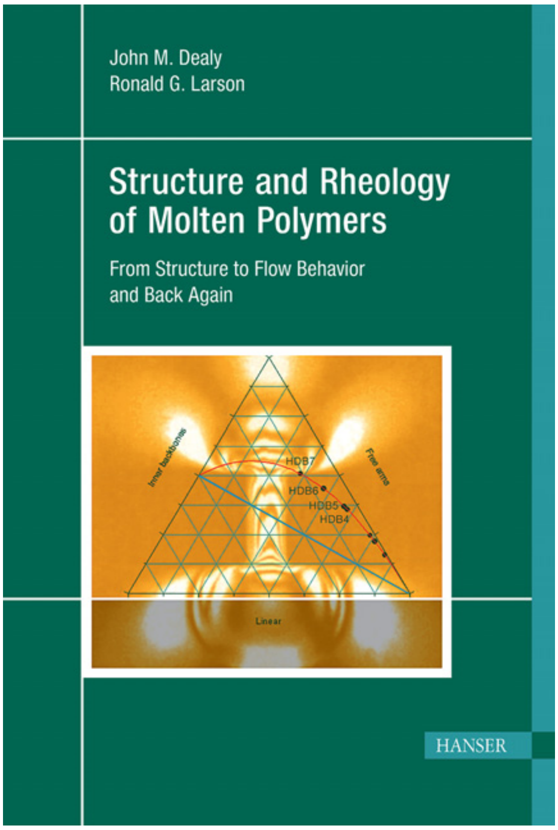


When I opened the book for the first time, I experienced one of the rare moments to say: Wow, what a nice book! It is about the present possibilities to predict rheology when the molecular structure is well known. Or alternatively, to use rheological data to obtain information about the structure of a molecule not known in all detail. Both ways have made significant progress over the last ten years. Better catalysts make molecules with a much more reproducible structures and the tube model with all its refinements makes measured and predicted properties converge better and better. The book is about polymer melts, except for the sections in the Chapter *structure of polymers* about intrinsic viscosity, osmometry, light scattering, and some data from shear and elongation experiments.

Everybody can use the book, even a newcomer in rheology, because it provides a condensed but clear introduction to polymer physics, chemistry, and experimental rheology. For the polymer scientist it is a rich source to look-up definitions of physical quantities, how to determine characteristic parameters, and to search for classical experimental papers.

The book has 12 chapters, each ending with a summary and a vast reference list. After the introduction, Chapter 2 (*structure of polymers*) introduces all parameters and methods used to characterise molecular size, polydispersity, and branching. In Chapter 3 (*polymerization reactions and processes*), chemistry is the topic. What role does the backbone play? What polymerization processes do exist and how do they affect the topology of the molecules? Exemplary for the polyethylene polymerization, the role of modern catalysts is outlined.

Linear viscoelasticity is split in two chapters: Chapter 4 (*fundamentals*) deals with the Maxwell model, time temperature superposition, and the determination and significance of relaxation and retardation spectra. The *behaviour of molten polymers* is discussed in the next chapter. Similar to Ferry's book, it is shown how the length of the chains and polydispersity act on relaxation moduli, dynamical data, and creep behaviour. The questions are answered, how do I properly determine the plateau modulus and how do the different critical molecular weights express themselves? The chapter then summarizes the peculiarities of copolymers and star polymers and closes with what one can learn from Cole-Cole and van Gurp-Palmen plots.

In the next two chapters, the *tube model* for linear polymers is introduced. Chapter 6 first discusses the Rouse-Büche model for unentangled polymers, then introduces the concept of entanglements, followed by the different modes of relaxation the chain explores after the tube has been strained. In Chapter 7 the limitations of the double reptation theory and peculiarities of long chain dynamics are discussed. It concludes with a compilation of literature values of tube model input parameters. It contains data such as monomeric friction coefficients, plateau moduli, and tube equilibration times. Very helpful is a table, comparing the tube parameters as defined by Fetters, Ferry, and Milner-McLeish.

Chapter 8 deals with a topic that is nowadays already part of many rheometer's software: How to *determine the molecular weight distribution* from rheology? This is indeed quite an important problem. The classical method of GPC discussed in Chapter 2 has its limitations. Naturally, it does not work for any insoluble polymer. Then, its ability to capture high molecular weight fractions is limited. But it is

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these minor contributions that have a great impact on the rheology and therefore, the rheological determination of the MWD is not a alternative method, but a complementary.

In Chapter 9, the tube model is extended to capture the dynamics of branched polymers, mostly model systems like symmetric and asymmetric stars, combs, and H-shaped molecules.

By far the largest chapter is devoted to *nonlinear viscoelasticity* (no. 10). First, the topic is addressed from a tube model's view. What implications do large deformations have on the tube model? Then, some classical constitutive equations are presented. The next section on classical non-linear step strain experiments cannot be complete without considering the predictions of the Doi-Edward theory. This theory is discussed even more profound in Chapter 11. Viscometric functions are shown with examples and discussed in terms of the tube model, the influence of polydispersity, and branching. In the two sections on experimental methods in shear and elongation, no figures and comparisons of rheometers are shown. However, the working equations are printed and the advantages and drawbacks of the methods discussed in the text. Also given are some widely used empirical rules for comparing and interconverting data, like the Cox-Merz, Lodge-Meissner, and Laun's for the first normal stress coefficient.

The experimental facts discussed in Chapter 10 are compared to the most recent constitutive equations in Chapter 11. Among these are tube models for linear and branched polymers, including all the modifications by Likhtman, Ianniruberto, and Marrucci that have been found necessary to capture the essence of the rheological behaviour. One section is devoted to the PomPom with all its revisions, because this constitutive model has been found most versatile to describe the non-linear rheology of highly branched polymers.

A book that claims to review the state of the art to bring into agreement the modelled and measure rheological behaviour of polymer melts has to conclude with a summary and with perspectives to what needs to be done to fill in the still existing gaps. This is the content of Chapter 12. It was mentioned that the book is useful also for newcomers. This is underline by a short appendix, listing some important tensors and presenting a table with the most important structural and rheological parameters of the most popular polymers.

*What is not in the book*

Since, first, it is not an experimenters handbook and, second, it is very difficult to model, there is not much said about flow instabilities occurring during rheological experiments, such as edge fracture, extrusion instabilities, secondary flow, shear banding, wall slip, compliance effects, and phase separation. However, all these points are at least mentioned at the appropriate locations in the book, so that the reader becomes aware of the problem and is guided to further reading.

*What did I particularly like about the book?*

It is very precise. Often in literature, one finds formulae with different prefactors, e.g. for the Graessley or Ferry notation of the relation between the plateau modulus and the entanglement molecular weight. The authors assigned different symbols to the two molecular weights and use them throughout and consequent, so that it is always clear, what is meant. The list of nomenclature comes with the equations were the symbol is used for the first time. This is no big deal with today's text programs, but it is nevertheless not self-evident. On each page is written where the references can be found. This is really helpful!

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**Bibliography**

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