# CONSTITUTIVE MODELING OF HIGHLY ORDERED SOLUTIONS OF MAIN-CHAIN LIQUID CRYSTALLINE POLYMERS CONTAINING HAIRPINS

## O. Matveichuk, J.J.M. Slot

Eindhoven University of Technology, Applied Analysis Department, Eindhoven, Netherlands

o.matveichuk@tue.nl

The ability of liquid crystalline polymers (LCPs) to form highly-ordered orientational states with extraordinary mechanical properties explains why LCPs are industrially used to produce strong fibres and are the subject of numerous studies in academic circles. LCPs, as all high-molecular weight polymers, show many characteristic timescales in their relaxation behavior where short respectively large timescales are to be associated with relaxation of small respectively large parts of the chain. The largest relaxation time is related to the relaxation of the chain as a whole and dominates its macroscopic behavior. This fact justifies the success of approaches in which only the longest relaxation time is taken into account [1]. For isotropic solutions of flexible polymers, therefore, theories based on rather coarse representations of the chain microstructure adequately describe the relaxation behavior of these systems. Examples of such theories are the Rouse and Zimm models of unentangled polymer liquids and the reptation model of entangled polymer liquids. The situation with solutions of LCPs, however, is much more complicated due to the fact that the persistence length of the chains is not negligible compared to their contour length. The persistence length is the distance along the chain over which orientational correlations persist. This leads to an anisotropic equilibrium state and a dependence of the distribution function on the nematic order parameter. Nevertheless, it is very useful to develop simplified models of LCP solution dynamics that only depend on a few microstructural parameters and allow one to study the effect of these parameters on the macroscopic properties of the LCP solutions in detail.

One of the most studied model of this type is the Doi rigid-rod model [2], [3]. The rigid-rod model, as its name suggests, neglects flexibility altogether and is applicable to LCPs for which the persistence length is of the same order as the chain length. In general, however, LCPs of sufficient length (molecular weight) are semi-flexible and hence form an intermediate case between that of rigid rods and completely flexible polymers. Consequently, models for semi-flexible LCPs were developed starting from both extremes. Either by extending the applicability of models for flexible polymers [1] or by relaxing the rigid constraint in the rigid-rod model by introducing the so-called slightly bending rod model [4], [5], [6].

For sufficiently long main-chain LCPs in highly-ordered orientational states it was de Gennes [7] who suggested that the loss of entropy would be partly recovered by the formation of so-called hairpins or kinks. The aim of the current work is to adopt the model of the Rouse-chain to describe the influence of hairpins on the rheological properties of solutions of highly-ordered semi-flexible LCPs in simple types of flow.

[1] Didier Long and David C. Morse. A Rouse-like model of liquid crystalline polymer melts: Director dynamics and linear viscoelasticity. J. Rheology. 46(1), 49-92 (2002)

[2] Doi M. Molecular dynamics and rheological properties of concentrated solutions of rodlike polymers in isotropic and liquid-crystalline phases. J. Polym. Sci., Polym. Phys. Ed. 19, 229243 (1981)

[3] N. Kuzuu M. Doi. Constitutive equation for nematic liquid crystals under weak velocity gradient derived from a molecular kinetic equation. J. Phys. Soc. Jpn. 52 34863494 (1983)

[4] F. Greco, M. Minale, G. Marrucci. Dynamics of stiff polymers with the slightly-bending-rod model. J. Non-Newtonian Fluid Mech., 76 351362 (1998)

[5] F. Greco, G. Marrucci. The tumbling or flow-alining nature of nematics as predicted from the Slightly Bending Rod molecular model. Liquid Crystals, Vol 22, No.1, 11-16 (1997)

[6] A. Subbotin. Dynamics of Slightly Flexible Rods in the Liquid Crystalline State. Macromolecules

26, 2562-2565 (1993)

[7] P. G. de Gennes, Polymer Liquid Crystals, Eds. A. Ciferri, W. R. Krigbaum and R. B. Meyer (Academic, New York) 1982, ch. 5.