Unusual nonlinear effects in the rheology of entangled polymer melts

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1. INTRODUCTION

It is well known that the dynamics of entangled polymeric liquids is very complex, both at equilibrium and under non-equilibrium conditions [1]. Several molecular mechanisms are believed to be responsible for such a complex behavior: reptation, contour length fluctuations, constraint release, stretch, and sometimes flow-induced inhomogeneitis. We here discuss the maxima in shear stress which are observed in the start up of shearing flows of entangled polymer melts with a complex structure, such as mixtures of branched molecules. More than one maximum can be observed, and the level of such maxima may change upon repeating the experiment after a not too long rest time. Unusual effects of the rest time have also been observed in concentrated solutions of linear polymers [2]. Repeated runs systematically reveal that, in order to reproduce the overshoot found in the virgin solution, the rest time must be much larger than the longest relaxation time.

2. START-UP BEHAVIOR OF COMPLEX SYSTEMS

We have performed start-up shear experiments on several styrene-butadiene (SBR) random copolymers in the biconical Mooney viscometer, and we observed that, while the linear SBR shows a normal behavior with a single overshoot, most branched SBR's exhibit additional maxima at higher values of the deformation γ. The first maximum at $\gamma \approx 2$ indicates that a large part of the polymer is not significantly stretched, and therefore generates the orientational overshoot predicted by the classical Doi-Edwards theory [1]. The second maximum at $\gamma >> 2$ is interpreted as due to internal segments of ramified structures that become stretched at large deformations. The γ values at which such secondary maxima occur seem to be independent of shear rate, consistently with the withdrawal mechanism originally proposed for the pom-pom model [3].

Additional evidence of complex behavior in branched SBR's emerges when repeating the start-up run after different rest times. Indeed, significant changes are observed in the level of the maxima, in particular with a reduction of the secondary maximum at high γ values. Such changes are reversible, however, thus excluding chemical degradation due to shearing. We know that the non-equilibrium structures created by branch-point retraction within the tube of the internal segments are long lasting, thus explaining the observed slow recovery of the start-up curve towards that of the virgin material. Furthermore we argue that, since the withdrawn structures remain quasi-permanently stretched, only their orientation varies during the second run, which might explain the observed changes in the levels of the maxima.

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