

Nonlinear Elongational Rheology of Unentangled Polystyrene and Poly(*p*-*tert*-butyl styrene) Melts

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Nonlinear rheology under uniaxial elongation was examined for unentangled melts of polystyrene (PS27; $M = 27\text{k}$, $n_K = 30$) and poly(*p*-*tert*-butyl styrene) (PtBS53; $M = 53\text{k}$, $n_K = 35$) having nearly the same number n_K of Kuhn segments *per* chain. For both materials, the steady state elongational viscosity η_E exhibited hardening and then softening on an increase of the Weissenberg number $Wi \geq 0.3$ ($Wi = \tau \dot{\epsilon}$, with τ and $\dot{\epsilon}$ being the longest relaxation time and the Hencky strain rate). For these unentangled melts, the hardening was unequivocally related to the finite extensible nonlinear elasticity (FENE), and the softening, to suppression of the FENE effect due to reduction of the segmental friction ζ occurring for highly stretched/oriented chains. Thus, the ζ -reduction, speculatively discussed for entangled melts, was experimentally confirmed for unentangled melts. The softening at high Wi was weaker for PtBS53 than for PS27 despite the similarity of their n_K values, which suggested that the magnitude of ζ -reduction depends on the chemical structure of the chain. Data for poly(*p*-alkyl styrene) will be also presented to confirm this dependence. Further details of this ζ -reduction, analyzed with the aid of the FENE bead-spring model modified for the ζ -reduction, are discussed in relation to the local motion of the chain necessary for adjusting ζ .