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Entangled linear, branched and hyperbranched polymers in shear flow

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Despite substantial progress in understanding the dynamics of long flexible polymers, several outstanding challenges remain. We address some of them. We discuss the response of well-characterized linear and branched (stars, combs, H) polymers to simple shear flow. The start-up stress behavior at high shear rates exceeding the inverse Rouse time, where according to tube-model theories polymer chains are oriented (and eventually stretched), is considered. We identify conditions under which combs are considered as effective diluted linear chains. We address the failure of stress-optical and Cox-Merz rules and the role of branching. Relaxation upon flow cessation is analyzed and a connection to convected constraint release is suggested. We apply the “probe rheology” approach to branched polymers diluted in polymeric matrix. Careful choice of matrix molar mass allows controlling constraint release effects. The shear response of asymmetric linear chain mixtures is also discussed in the context of recent studies in uniaxial extension suggesting enhancement of extensional viscosity. Entanglement-like effects are observed in dendronized polymers with branches below the entanglement limit, which interpenetrate to reduce inherent density heterogeneity.

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