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Tightening the noose on tube models: a priori determination of equilibration time and other tube model parameters for 1,4-polybutadienes PRIYANKA DESAI, RONALD LARSON, University of Michigan, XUE CHEN, Dow Chemical Company, SEUNG JOON PARK, Korea Polytechnic University — Linear viscoelastic G' and G" master curves for multiple linear, star, H, and comb 1,4-polybutadienes from the literature were compared and found with only one exception to agree well in the high frequency region, where G' and G" exceed the plateau modulus, irrespective of molecular weight and branching structures. This agreement occurred despite variations of up to an order of magnitude in the horizontal shift factors used for generating master curves, probably due to small variations in the percentage of 1,2 linkages, which ranges from 6-10% for typical 1,4-polybutadienes. Fitting high frequency data to the Rouse theory yields a "universal" equilibration time of around $\tau_e = 3.7e-07$ s at 25 C, regardless of chain architecture. From a study by Carella et al. (Macromolecules 17:2775, 1984), the plateau modulus for 1,4-polybutiene is expected to vary by only 2% for 1,2 content ranging from 0.06 to 0.10, and a similar variability of the entanglement molecular weight over this range can be inferred for this range of 1,2 content. Accordingly, for typical 1,4-polybutadienes, with 1,4 content ranging form 6-10%, all three canonical parameters of the tube model can be taken as fixed within a tight range, for 1,4-polybutadienes of any architecture, thus providing tight constraints on parameter adjustments that might be used to fit theories, such as tube theories, to rheological data.

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