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Relaxations of star-shaped polystyrene melts approaching the colloidal limit KYLE JOHNSON, University of Michigan, EMMANOUIL GLYNOS, Foundation for Research and Technology-Hellas, GEORGIOS SAKELLARIOU, University of Athens, PETER GREEN, University of Michigan — The dynamics of star-shaped polystyrene melts with functionalities ranging from 8<f<64 and arm molecular weights ranging from 9 kg/mol <M<80 kg/mol were investigated using small amplitude oscillatory shear measurements. The frequency dependent storage, G', and loss, G", moduli were measured in the linear viscoelastic regime in order to characterize the terminal relaxation behavior of the macromolecules. Our studies reveal gradual, low-frequency deviations away from the Milner-McLeish theory for arm retraction indicating more elastic behavior as functionality is increased. The magnitudes of these deviations diminish with increasing arm molecular weight. These elastic deviations are consistent with the emergence of a relaxation representing cooperative structural rearrangements and colloidal behavior. Our results indicate that changes in the size of the core region for low molecular weight arms leads to a transition in the dynamics from an arm retraction mechanism to a cooperative, structural relaxation mechanism.

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