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Long-Time Dynamics in Polymers: Experimental Results[1]

SINDEE SIMON, Department of Chemical Engineering, Texas Tech University

The long-time dynamics in several polymeric systems have been investigated with a focus on the relationship between the bulk and shear viscoelastic responses. Materials studied include polystyrene, a three-arm star polystyrene, and two polycyanurates of different crosslink densities. A custom-built pressurizable dilatometer has been used to measure the time-dependent bulk modulus, as well as the pressure-volume-temperature behavior in these materials. The temperature-dependent shift factors are used to test the TV^{γ} thermodynamic scaling law proposed in the literature for segmental relaxation times. The thermodynamic scaling law successfully reduces the data for all of the materials; however, T - Tg scaling also successfully reduces the data and differences in implications of the two scaling approaches will be discussed. Comparison of the retardation spectra for the bulk and shear responses shows that at extremely long times, the chain mechanisms available to the shear response are not available to the bulk; for times related to the glassy dynamics, the two responses have similar slopes, indicating that they may have similar underlying molecular mechanisms, but the magnitudes are different, a finding that remains to be explained.

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