ELONGATIONAL VISOCOSITY OF A POLY(STYRENE-B-2-VINYLPYRIDINE) BLOCK COPOLYMER FORMING SPHERICAL MICROPHASE-SEPARATED STRUCTURE

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Block copolymers generally form microphase-separated structures, and thus exhibit characteristic linear and nonlinear rheological properties that reflect their structures, which is essentially different from homopolymers. Polystyrene (PS) and poly(2-vinylpyridine) (P2VP) have the same Kuhn segment size, the same glass transition temperature, and nearly identical melt viscoelastic properties, and hence poly(styrene-*block*-2-vinylpyridiene) (PS-*b*-P2VP) is a model block copolymer suitable for various linear and nonlinear rheological investigations. In fact, Takahashi et al. have experimentally examined the linear rheology and viscosity under shear flow of PS-*b*-P2VP melts with various molecular weights and compositions.[1,2] Over the past two decades, with the development of measurement instruments, the elongational viscosity of polymer melts and solutions has been extensively examined and their molecular picture is becoming better understood.[3] However, there are still limited reports on the elongational viscosity of block copolymers, and the full picture has not yet been clarified. In this study, we experimentally investigated the elongational viscosity of a PS-*b*-P2VP sample that forms a spherical microphase-separated structure. The PS-*b*-P2VP sample used in this study (purchased from Polymer Source) has a weight average molecular weight M_w = 101 kg/mol and volume fraction of P2VP Φ_{P2VP} = 0.092. This sample is hereafter denoted by SP009, reflecting Φ_{P2VP}. Disk-shaped samples of SP009 were prepared by hot pressing and annealing, and their elongational viscosity was measured by a filament stretch rheometer VADER1000 (Rheo Filament) at various strain rates $\dot{\varepsilon}$ (= 0.001~0.1 s^{-1}) at 200 °C. The terminal relaxation time τ_d of SP009, which originates from the relaxation of the spherical phase-separated interface determined by linear viscoelastic (LVE) measurements, is approximately 10^3 s at 200 °C, and hence the Weissenberg number Wi (= $\dot{\varepsilon}\tau_d$) corresponds to ca. 1~100. SP009 exhibits a steady-state elongational viscosity $\eta_E(\dot{\varepsilon})$ that is almost two order of magnitude lower than that expected from LVE even at Wi = 1, and $\eta_E(\dot{\varepsilon})$ decreases with increasing Wi, indicating the strain softening. Moreover, Wi dependence of $\eta_E(\dot{\varepsilon})$ itself is similar to that found in homopolymer melts.[3] In the presentation, we will discuss the origin of the strain softening observed in SP009.

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