Shear and Extensional Rheology of Controlled Microstructure Poly(lactic acid) Polymers

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In this study, a series of controlled microstructure poly(lactide) polymers (PLAs) were synthesized by using novel ring-opening polymerization methods that utilize chiral main group catalysts for enantioselective polymerization of lactide (Douglas and Mehrkhodavandi, Angew. Chem. Int. Ed. 47, 2290, 2008). The polymers made are of polydispersity slightly higher than 1 (nearly monodisperse) and ratios of L to D enantiomeric monomers of 100:0, 75:25, 50:50, 25:75 and 0:100. The rheological study includes determination of zero shear viscosity and its relationship with the molecular weight, the relaxation spectrum and its relation with molecular weight characteristics, plateau modulus and other important rheological parameters that are helpful in predicting the linear viscoelasticity of PLA polymers (J.R. Dorgan, J. Janzen, D.K. Knauss, et. al., Journal of Rheology, 49(3), 607-619 (2005)). Emphasis is also placed on the uniaxial melt behaviour of these polymers. At low temperatures, significant strain hardening is observed which gradually disappears with increase of temperature and decrease of Hencky strain rate. The origin of the strain hardening is investigated from (i) the point of view of flow induced-crystallization using DSC and polarized microscopy as PLAs are known to crystallize extremely slowly and (ii) from the point of view of polymer melt dynamics in terms of the relative magnitudes of the characteristic times of reptation and deformation.