Living Polymerization of α-Methylstyrene in Tetrahydrofuran Followed by Dynamic Light Scattering Near Its Polymerization Temperature

J. Ruiz-Garcia
Instituto de Física
Universidad Autónoma de San Luis Potosi
Alvaro Obregón 64
San Luis Potosí, S.L.P. 78000, México

R. Castillo
Instituto de Física
Universidad Nacional Autónoma de México
P.O. Box 20-364
México, D.F. 01000, México

We present dynamic light scattering measurements of the living polymerization reaction of α-methylstyrene, initiated by sodium naphthalide in tetrahydrofuran, near its polymerization temperature. Light scattering measurements were obtained after at least 180 min. of thermal stabilization to assure complete relaxation of the sample. We followed the polymerization reaction as a function of the temperature, where we used the correlation functions to detect the change on polymer size and to estimate the diffusion coefficients. Our correlation times are not too large to prevent degradation of the sample, typically between 5-7 min. We present a cooling-heating cycle for a sample. We found that the diffusion coefficient decreases as the temperature is lowered below the polymerization temperature, as expected, since the polymer grows on cooling. The diffusion coefficient does not follow the same track values on the heating run as on the cooling run, however, remaining at somewhat higher values. We also obtained the hydrodynamic radius at the lowest temperature reached in our experiment, using the well known Stokes-Einstein equation and using estimated viscosity values. Our R_h values lie between 3-4 nm. Those values are comparable with the 3.66 nm obtained for the dimeric form of living polystyrene in benzene. In addition, our average molecular weight, for complete conversion of monomer into polymer, is 1.7×10^3, of the same order of magnitude as the experiments of polystyrene in benzene, but we used a more polar solvent. Our results suggest, that the difference on the diffusion coefficient on the cooling-heating cycle is due to the formation of associated polymeric forms, which might not necessarily be dimers, because in our case living poly-α-methylstyrene is active in both sides of the chain.