232d Study of Single-Site Linear Low- Density Polyethylene Liquids Using Inverese Gas Chromatography and Molecular Dynamics Simulation

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Two thermodynamic quantities, zero-pressure-weight-fraction Henry's constants (H_{12}^{0}) and infinite-dilution-weight-fraction activity coefficients (Ω_1^{∞}), were measured for 12 hydrocarbon solvents in a series of single-site octene-based linear low-density polyethylenes (ss-LLDPEs) with different branch contents using inverse gas chromatography (IGC) over the temperature range from 170 to 230 ^{0}C. The IGC results showed that H_{12}^{0} of the solvents with low and medium-boiling points (50 – 150 ^{0}C) exhibited a minimum in the branch content range of 0 to 20 branches per 1,000 backbone carbons and became independent of branch content over a higher range from 20 to 87. For the solvents with high-boiling points (150 – 250 ^{0}C), H_{12}^{0} was insensitive to branch content at all. As temperature was increased, the observed behavior became more pronounced for the highly volatile solvents and propagated to solvents with medium volatility. The above observation is mainly attributed to the relatively more favorable interactions between the solvents and the polymers with branch contents less than 20, as quantified by the measured Ω_1^{∞}. Calculations of the free volumes of comparable octene-based ss-LLDPE models with different branch contents using molecular dynamics simulation suggested that the volume fraction of spherical free volume holes with radii larger than 1.5 Å decreased with increasing branch content, leading to the observed of Ω_1^{∞} behavior.