Poly(ethylene terephthalate) (PET) is one of the most important commercial crystalline polymers. Extensive work has been done (through X-Ray based techniques) to understand the morphology development during crystallization and melting of PET with an emphasis on developing highly crystalline PET. Another area of interest targets improved melt stability of PET using various multi-functional epoxies for chain extension. Understanding of crystallization index and rate of crystallization is important to the development of highly crystalline PET. Usually, the reactivity differences between various epoxides towards polymer ends are inferred through acid value, molecular weight and intrinsic viscosity of the polymer. In the present work, we have established the use of crystallization index of PET as an additional parameter to predict the reactivity of various epoxies with PET. The experimental results thus obtained are supported by the bond order based model calculations.