

A Model for the Diffusion of Polymeric Melts based on the Generic van der Waals Equation of State and the Free Volume Theory

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In this paper, we investigate the dynamics of diffusion of polymer melts by developing a phenomenological model based on the integral equation theory for site-site pair correlation functions, the generic van der Waals equation of state, and the modified free volume theory. The integral equations are used to find the pair correlation functions necessary for the generic van der Waals equation of state. This later, in turn, is used to calculate the self-diffusion coefficient on the basis of the modified free volume theory. A random distribution is assumed for minimum free volumes for monomers along the melt chains. Actually, a stretched exponential is used for the distribution function. For polymer melts of N monomers, the N dependence of the self-diffusion coefficient is N^{-1} for small values of N , as predicted by the Rouse theory. But in the range $2.3 \leq \ln N \leq 4.5$, the N dependence smoothly crosses to N^{-2} , as predicted by the reptation theory. For $\ln N > 4.5$, the N dependence of the self-diffusion coefficient becomes $N^{-2-\delta}$ ($0 < \delta < 1$), which is consistent with experimental results on polymer melts in the same range. This semi-empirical N dependence of diffusion allows also the prediction of the dependence of the self-diffusion coefficient on temperature. The theory is successfully tested against experimental and simulation data on polyethylene and polystyrene melts.