MULTICOMPONENT DIFFUSION AND PHASE SEPARATION IN ASYMMETRIC TERNARY POLYMER SYSTEMS

by

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ABSTRACT

The prediction of diffusion coefficients in multicomponent systems, and particularly in polymer systems, has been the subject of many theoretical studies. A common problem with these approaches is that, under some circumstances, they violate the material balance constraint and give non-physical predictions. Various friction-based theories have been tested for ternary systems, and negative concentrations were observed for the balancing, third component. The non-physical result is caused by inequality in the fluxes of the major components when the concentration of the third component is small. The model constructed by Price and Romdhane is an improvement, but it requires that the self-diffusivities of the various components to be inversely proportion to their molecular weights. An empiricism, the proportional flux method, is recommended to avoid non-physical results that retain the desirable features of the theoretical models. The method has been partially verified by molecular dynamic simulations.

Most simulations of diffusion in ternary systems undergoing spinodal decomposition have been limited to systems where the component diffusivities are either equal or displaying one dominant component. The case of unequal diffusivities has proven more difficult because standard calculations can give non-physical results that violate a material balance constraint. Presented in this work is a solution technique that is similar computationally to the standard method yet allows diffusion coefficients to be set arbitrarily. The ternary extension of the Cahn-Hilliard equation is coupled with the proportional flux method to predict phase separation morphologies. The method gives results equivalent to the standard technique for the case of equal diffusivities and reduces to Fickian diffusion when the mixture is ideal. A two-dimensional simulation of an asymmetric polymer-polymer-polymer system reproduces an experimentally observed bimodal distribution of dispersed-phase particle sizes for a system where the component diffusivities differ by two orders of magnitude. The ripening exponent for the larger particles is near the expected value of 0.33; however, the ripening exponent for the smaller particle only about 0.1. The method was applied to a polymer/polymer/solvent

system where the solvent not only had a much higher diffusivity but also had different interaction parameters with the polymers, $\chi_{13} = 0.2$ and $\chi_{23} = 0.5$.

The ability to treat asymmetric systems has opened up the possibility to investigate different classes of problems. The reaction induced phase separation was investigated in this dissertation. A reactive extension of the technique developed earlier to resolve the flux imbalance that results from high difference in diffusion coefficients was utilized. The workability of this approach was demonstrated on the example of high impact polystyrene. The final morphology is a continuous polystyrene phase and a discrete rubber phase where the rubber particles contain polystyrene occlusions. The morphology is modeled for an agitated batch reactor. Simulations of a quiescent batch polymerization also give a discrete rubber phase. This is contrary to reports in the early patent literature, the difference being attributed to a reduction in diffusivity and to cross linking of the rubber that are not considered in the current model