Thermodynamic Analysis on the Phase Behavior of Copolymer Blends: An Equation of State Approach

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A new and simple model of copolymer blends based on the Prigogine-Flory-Patterson's equation of state theory is presented to quantitatively understand the effect of comonomer on the lower critical solution temperature (LCST) behavior of copolymer blends. The free volume contribution was introduced to the Flory-Huggins interaction parameter χ_{AB} according to Patterson's treatment. The new model explains that the intramolecular interaction within copolymers contributes to the free volume term as well as to the interaction term. Unlike its contribution to the interaction term, the repulsion within copolymers is not always favorable to the free volume term. The interaction term is proportional to the change in the net interaction caused by the presence of comonomer. The free volume term is controlled by the two factors: the intramolecular interaction and the relative magnitude of the characteristic parameters of comonomer.

The applicability of the model was examined for several blend systems. For poly(vinyl methyl ether) (PVME)/styrenic copolymer and polymethacrylates/vinyl chloride-vinyl acetate copolymer blends, segmental contact energy parameters were obtained by fitting the LCST data to the new model. The variation of the χ_{AB}/C_A parameter calculated at a given temperature was in good agreement with the variation of the LCST with the copolymer composition and the type of comonomer. The free volume term was significant for correlating the LCST data with the χ_{AB}/C_A parameter, which illustrated the advantage of the new model over a binary interaction model based on the Flory-Huggins theory.

The new model proposed in this study offers a quantitative guide on how to select the

comonomer that gives a favorable effect to raise the LCST of polymer blends. This is possible when one considers quantitatively the effect of comonomer on the two factors, the interaction and free volume terms of the χ_{AB}/C_A parameter.

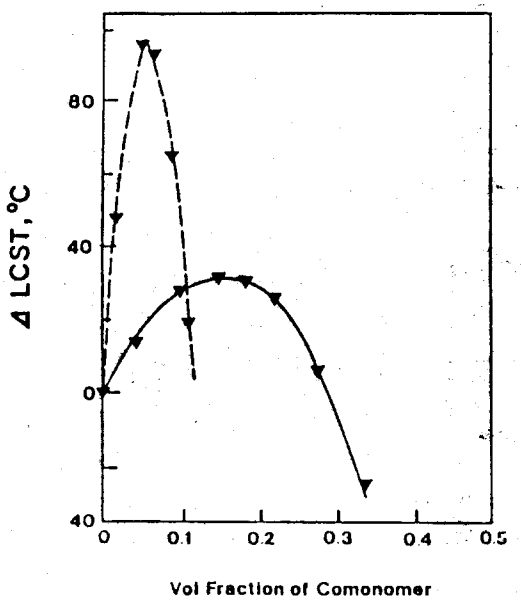

Figure1. Variations of the LCST with the copolymer composition for PVME/ styrenic copolymer blends. The LCST of PVME/PS is chosen as a reference: the solid line for SMMA series; the broken line for SAN series.

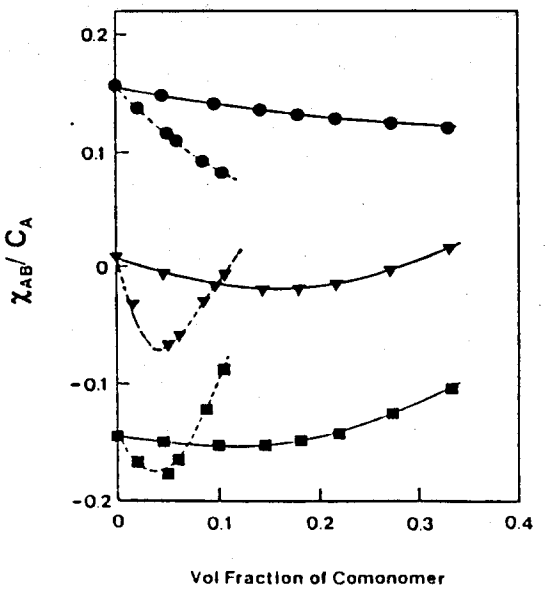

Figure 2. Variation of the interaction (■) and free volume (●) contributions to χ_{AB}/C_A parameter (▼) as a function of copolymer composition at the LCST of PVME/PS blends.