

Volume 19 Number 1 1994

ISSN 0079-6700

PROGRESS IN  
**POLYMER  
SCIENCE**

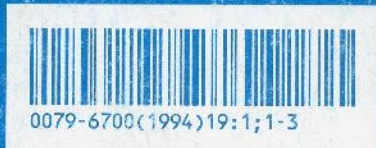
An International Review Journal

Editor: **O VOGL**  
*Polytechnic University,  
New York, USA*

Associate Editor: **G D JAYCOX**  
*E. I. du Pont de Nemours & Co.,  
Wilmington, USA*



**PERGAMON PRESS**  
Oxford New York Seoul Tokyo



0079-6700(1994)19:1;1-3



## THERMODYNAMICS OF POLYMER SOLUTIONS AND MIXTURES

YOSHIYUKI EINAGA

*Department of Polymer Chemistry, Kyoto University, Kyoto 606-01, Japan*

**Abstract** — A review is provided for the present situation concerning theoretical predictions of phase equilibria in polymer solutions. Special attention is paid to ternary systems consisting of two polymers and one solvent or of one polymer and two solvents. A survey of the experimental data on various ternary systems has revealed that phase separation behavior is significantly and subtly affected by three interaction parameters for each pair of components, and that a quantitative description of the phase relations requires a very accurate expression of the interaction parameters as a function of temperature, composition of the system, molecular weight of the polymer, and so forth. One promising approach has recently been developed and is based on classical thermodynamic relations of general validity. This is described in some detail. It will be shown that this approach is useful for the characterization of thermodynamic properties of a given ternary system as a function of all relevant variables, and that it allows for the prediction of phase equilibrium behavior with sufficient accuracy.

### CONTENTS

1. Introduction	1
2. Phase diagrams of ternary systems	3
3. Expressions for the Gibbs free energy of mixing	8
3.1. General formulation of $\Delta G$	8
3.2. Determination of the interaction function	11
4. Interaction functions	13
4.1. Concentration, molecular weight, and temperature dependence of the binary interaction parameters	13
4.2. Empirical expressions of binary interaction parameters	19
5. Calculated phase diagrams	23
6. Concluding remarks	26
References	27

### 1. INTRODUCTION

For nearly half a century, the renowned Flory–Huggins theory has been played a central role in our understanding of the thermodynamics of polymer–solvent and polymer–polymer mixing and demixing. This theory was presented independently by Huggins<sup>1,2</sup> and Flory<sup>3,4</sup> in the early 1940s. The Gibbs free energy expression derived from this theory has been applied to a wide variety of systems in which at least one of the components is a polymer. These include binary (or quasi-binary) systems consisting of a solvent and a monodisperse (or a polydisperse) polymer,<sup>5–10</sup> ternary (or quasi-ternary) systems including solutions of polymer mixtures,<sup>10–13</sup> a single polymer in mixed solvents<sup>14–16</sup> and mixtures consisting of three chemically distinct polymers.<sup>17</sup> Polymer species examined for their phase equilibrium behavior, include linear or branched homopolymers, random or block copolymers, water-soluble or insoluble polymers, and so forth.<sup>18–20</sup>