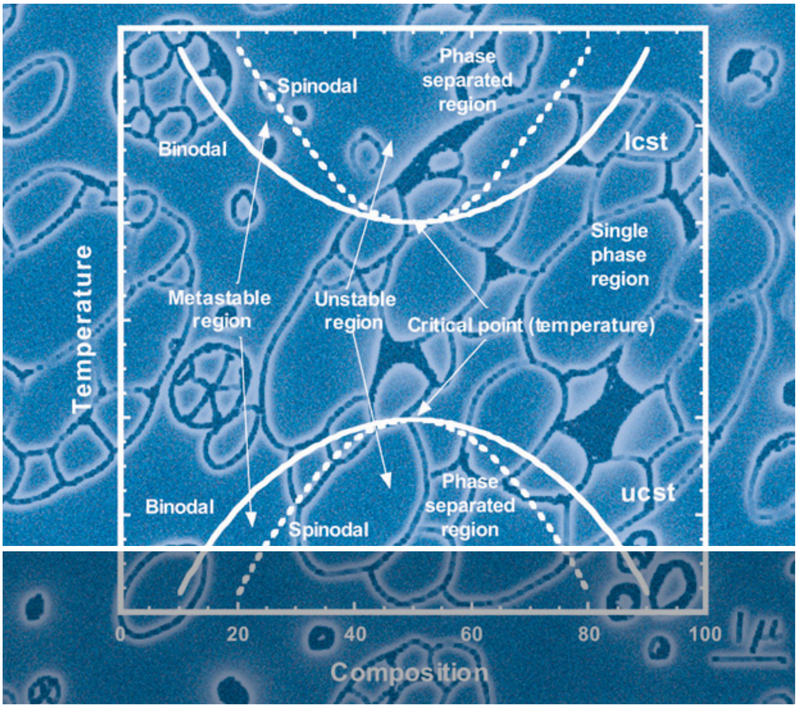
Lloyd M. Robeson

Polymer Blends

A Comprehensive Review



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To my wife, Saundra, whose support and perseverance is greatly appreciated; and to my mother who instilled into me the importance of education at an early age.

Preface

The field of polymer blends has been one of the most prominent areas of investigation in polymer science in the past several decades. In 1967, when the author started his professional career, polymer blend technology was virtually at the beginning with miscibility in polymer blends believed to be extremely rare if not basically impossible. The technology involved with the compatibilization of immiscible polymer blends was yet to be developed. The fundamental relationships covering the thermodynamics of polymer blends were at least partly developed but concepts including equation of state thermodynamics did not exist. The field of polymer blends has an analogy with metal alloys, and the technology development over the past four decades has well-established the principles and practice leading to significant commercial successes. The search for new materials to solve the materials needs for emerging applications now often relies on polymer blend solutions. With four decades of research in this area by the author, a perspective of the developments in this technology is hopefully presented illustrating the significant developments as the polymer blend technology matured.

A prior book on polymer-polymer miscibility (Academic Press: 1979) was coauthored, and this author did not remember how time-consuming a book preparation can be and embarked on this book almost five years ago resulting in a lot of long nights and weekends. This book covers the broader field of polymer blends and is both an introduction and a reference text. As an introduction it does not cover the subject material in the depth found in references dedicated to specific subsets of the field. As a reference text, sections of the book are highly referenced and limited in detailed discussion and may unfortunately be boring reading. While a number of excellent books exist on polymer blends, it is hoped that this book provides a broad overview of the field with seminal references as well as recent references of interest. Many of the available books on polymer blends are edited texts offering detail in the subject areas covered. Several excellent authored texts are also available covering specific aspects of polymer blend technology although generally not as comprehensive and also not recent. Hopefully, this book can cover the entire field and update the many recent contributions to the subject.

The author has split his career at two companies (Union Carbide: 1967–1986; Air Products and Chemicals, Inc.: 1986–2007). The author wishes to acknowledge the strong commitment of both companies to technology and the ability to conduct research in an atmosphere dedicated to strong professional development. The supportive management in both companies provided the encouragement to be involved with the broader technology community and ultimately undertake the significant effort involved with preparation of the polymer blend reference texts. Over the years, the author has been able to meet and discuss the subject area with the leaders in the field. One key leader that deserves special acknowledgement is Dr. Donald R. Paul of the University of Texas. His contributions to the field are well-documented in this text as well as specific figures from his publications. His review of the manuscript offered many important corrections and additions. Other prominent investigators in the field whose input and discussions over the years is greatly appreciated include Drs. M. T. Shaw and O. Olabisi (coauthors of the first book noted above), Drs. F. E. Karasz, W. J. MacKnight, J. W. Barlow, J. E. Harris, J. E. McGrath, R. A. Weiss, A. Eisenberg, J. V. Koleske, L. A. Utracki, L. H. Sperling, M. M.˜Coleman, C. B. Bucknall, G. Groeninckx, D. G. Baird, L. P. McMaster, M. Matzner, Ph. Teyysie, L. M. Maresca, E. M. Pearce and my apologies for not noting the many others which have influenced the content of this book. Specific figures were kindly obtained from Drs. R. J. Spontak and D. G. Baird offering important morphological illustrations so important to a book on polymer blends. Rough drafts of this book were utilized in the CHE/CHM/MAT 485 course on Polymer Blends and Composites taught at Lehigh University. The comments of the students (not always favorable and rightfully so) were quite helpful in the preparation of the book in the final version. The author wishes to acknowledge the helpful comments and suggestions made on requested reviews of various chapters of the book by Drs. L. H. Sperling, M. T. Shaw, O. Olabisi, F. L. Marten, and C. D. Smith. The assistance of Linda Schanz in providing computer process related advice and figure reproduction is also greatly appreciated.

Finally, I wish to acknowledge the important contribution of my family. My mother taught me mathematics and reading at an early age (before elementary school) and my father instilled in me the ‘midwestern work ethic’ (although I wasn’t always sure I wanted to learn it). That provided the basis for obtaining the skills necessary to accomplish the task of this endeavor. My wife, Saundra, has always been very supportive of the long hours and tables filled with references around the house as I prepared this book. Without that support, this book would never have been completed.

Spring 2007 Lloyd M. Robeson

Contents

1 Introduction

1.1 General Overview

The technology of polymer blends has been one of the major areas of research and development in polymer science in the past three decades. Judging from the number of publications, patents, and PhD theses in this area, it continues to maintain a prominent position. The analogy of polymer blends (which can also be referred to as polymer alloys) with similar earlier developments in the field of metal alloys is an interesting comparison. The utility of polymer blends in commerce has resulted from the noted emphasis and understanding of polymer blend technology. It has been well-recognized that polymer blends offer a key option in solving emerging application requirements.

The advantages of polymer blends versus developing new polymeric structures have been well-documented. The ability to combine existing polymers into new compositions with commercializable properties offers the advantage of reduced research and development expense compared to the development of new monomers and polymers to yield a similar property profile. An additional advantage is the much lower capital expense involved with scale-up and commercialization. Another specific advantage of polymer blends versus new monomer/polymer compositions is that the blends can often offer property profile combinations not easily obtained with new polymeric structures. In the rapidly emerging technology landscape, polymer blend technology can quickly respond to developing needs, much faster than the time consuming R&D involved with new monomer/polymer development. The technical response to emerging needs is now first directed at polymer blend technology to determine if such needs can be met compared to development of wholly new polymeric compositions.

The role of polymer blend technology is pervasive in the products of our everyday life. Tires are comprised of elastomer blends, impact modified polymers are among the largest volume polymers (impact polystyrene, ABS, impact modified polypropylene, impact modified PVC), engineering polymer blends are used in appliances, electronics and automotive applications, and polyolefin blends are utilized for a myriad of film applications. The new emerging technologies of the future involving polymeric materials often employ polymer blends designed to deliver unique properties.

The types of polymer blends are quite varied and comprise many diverse combinations of polymeric materials of both academic and industrial interest. The primary differentiation of polymer blends involves their phase behavior; specifically, miscibility versus phase separation. Miscibility is related to mixing approaching the molecular dimension scale such that the properties observed are that expected of single phase materials. Miscibility does not imply ideal mixing at the molecular scale. Miscibility was initially believed to be an extremely rare observation and, in fact, most random combinations of binary blends are indeed phase separated. However, many miscible combinations have been noted and the rationale for miscibility is well-established. The primary advantage of miscible versus phase separated polymer blends is the blend property profile, which is generally intermediate between that of the

Table 1.1: Types of Polymer Blends

Elastomer blends	Engineering polymer blends
Emulsion blends	Crystalline-crystalline polymer blends
Impact modified polymers	Crystalline-amorphous polymer blends
Thermosetting polymer blends	Biodegradable polymer blends
Molecular composites	Reactive compatibilized blends
Liquid crystalline polymer blends	Polyolefin blends
Interpenetrating polymer networks	Isomorphic polymer blends
Polyelectrolyte complexes	Water soluble polymer blends
Recycled polymer blends	Core-shell polymers systems
Polymer blend composites	Electrically conducting polymer blends
Block copolymer-homopolymer blends	Blends comprising natural polymers

unblended constituents (specifically, mechanical properties). Often, phase separated systems exhibit mechanical incompatibility due to the weak adhesion at the interface between the phases. This is not always the case, and specific methods are available to alleviate the interfacial adhesion deficiencies which will be detailed later.

The technology involved with polymer blends includes a multitude of polymer alloy compositions including elastomer blends, engineering polymer blends, impact modified polymers, crystalline polymer blends, glassy-crystalline polymer blend combinations, reactive compatibilized blends, liquid crystalline polymer reinforced blends, and molecular composites. These and other types of polymer blends are listed in Table 1.1. Impact modified blends are generally composed of a continuous matrix of a rigid polymer with a minor phase of an elastomer. Combinations of crystalline polymers with glassy polymers can yield useful property profiles, such as those required for automotive panel applications, by combining chemical resistance, toughness and heat resistance attributes of the individual components. Blends of polyolefins have been commercially utilized for over four decades offering an optimization of properties not readily available with any individual polyolefin. Elastomer blends are common in tire compositions yielding a combination of properties not capable with the unblended components. Emulsion blends are commonly employed for adhesive and coating applications.

The understanding of the potential of polymer blend technology to design specific compositions to meet application requirements is of primary importance. Individual polymers have a singular property profile capable of meeting only a limited number of applications. The applications potential for any polymer can be greatly enhanced by employing the principles of blend technology. This book is designed to provide an overview of this technology such that the polymer scientist/engineer can employ these principles in designing polymer blends for meeting present and emerging application requirements.

As this field has been one of the major areas of investigation in polymer science in the past three decades, a number of books have been published on this subject as well as detailed reviews [1–32]. Additionally, books covering the specific areas of interpenetrating polymer networks (IPNs) [33–35] and impact modification [36–38] are listed.

1.2 Historical Review

The earliest utilization of polymer blends occurred long before synthetic polymers were available. Natural products (e.g., resins, natural rubber, cellulose) of polymeric nature were combined to achieve desired coating and adhesive materials. With the initial commercialization of modified natural products such as nitrocellulose in the mid 1800s, examples of polymer blends have been noted. A natural resinous product, shellac, was added to nitrocellulose to improve the coating toughness. When phenolic thermosetting polymers were introduced in the early 1900s, blends were also developed to improve the properties. A specific example involved phenolic blends with vulcanized natural rubber representing one of the first applications of interpenetrating polymer networks [39]. These compositions were used for improved phonograph records over the very brittle phenolic systems.

One of the early commercial blends comprising synthetic polymers involved poly(vinyl chloride) PVC and butadiene-acrylonitrile (nitrile rubber: NBR) copolymer elastomers. This blend has been commercially available since the early 1940s [40,41] and is still available today. This blend has been shown to be miscible [42] with a single broad glass transition temperature implying less than ideal miscibility. The addition of butadiene-acrylonitrile elastomers (uncrosslinked) to PVC yields a permanently plasticized PVC resistant to plasticizer migration and utilized for wire and cable jacketing, low voltage primary insulation, oil containments liners, pollution control pond liners, fuel hose covers, printing roll covers, gaskets, conveyor belt covers and various applications requiring permanence of the plasticization additive for PVC.

Another polymer blend with large present commercial utility involves rubber modification of polystyrene (impact polystyrene) and acrylonitrile-styrene copolymers (commonly referred to as ABS: acrylonitrile-butadiene-styrene). The early commercial blends were simple mixtures of polystyrene and polybutadiene or styrene-butadiene elastomers (both uncrosslinked). While impact modification was achieved, the efficiency of rubber incorporation was limited. It was found that polymerization of styrene in the presence of rubber yielded significant properties improvements over simple blends. The polymerization process proceeds to a point where the styrene-polystyrene-rubber ternary mixture phase-separates. With agitation commonly employed during the polymerization process, there is a phase inversion at the point of phase separation resulting in discrete rubber particles containing styrene-polystyrene occlusions. The resultant particle size and distribution, degree of polystyrene occlusion in the rubber particle, crosslinking of the rubber phase and polystyrene grafting to the rubber are important factors in the efficiency of impact modification [43]. Other impact modified systems commercial for almost four decades include polyolefin elastomer (ethylene-propylene rubber) modification of polypropylene and impact modified PVC. Emulsion polymerization of acrylates (e.g., poly(methyl methacrylate) and copolymers) in the presence of rubber (polybutadiene or styrene-butadiene copolymers) yields discrete particles which (after drying) can be melt blended with PVC to yield the desired impact modification. PMMA and specific acrylic copolymers offer excellent adhesion to PVC (as partial miscibility can be achieved) thus assuring good adhesion between the phases.

The major interest in polymer blend technology emerged in the late 1960s. One of the catalysts for this interest was the commercialization of poly(2,6-dimethyl-1,4-phenylene oxide) (PPO)/polystyrene blends by General Electric under the tradename Noryl®. It was recognized that PPO/polystyrene blends were miscible and thus offered a property profile intermediate between the constituents (weight averaged) over the entire composition range [44]. The addition of PPO to polystyrene increased the T_g (thus heat distortion temperature), improved the impact resistance and increased the tensile strength. Another important property achieved was the improved flammability resistance of polystyrene with addition of PPO. The ability to pass the important UL-94 (Underwriter Laboratories flammability test) requirements for appliance applications with lower cost phosphate based flame retardants allowed for rapid market acceptance of this blend. Commercially, impact polystyrene is employed in the blend with PPO to achieve increased toughness. As a myriad of price/performance variations exist as a function of blend composition, it became apparent that polymer blends (particularly with achievement of miscibility) could potentially offer a large number of different commercial products. This recognition resulted in greatly increased efforts in industrial R&D laboratories directed towards polymer blend technology. The miscible nature of the PPO/polystyrene blend presented the possibility that miscible polymer systems may be more prevalent than initially believed. Academic interest in polymer blend phase behavior thus emerged resulting in intense investigations in a number of academic institutions.

While the interest in finding new miscible polymer combinations emerged and it was well demonstrated that miscibility was much more prevalent than initially perceived, additional interest in understanding the nature of phase separated polymer blends also surfaced. Both academic and industrial laboratories recognized the importance of phase separated polymer blends as novel compositions offering unique/useful property profiles. As phase separated polymers often exhibited poor to limited mechanical compatibility, concepts of compatibilization emerged as noted in Table 1.2. A number of important concepts and methods for studying polymer blends were developed several decades ago and will be highlighted in this treatise.

The importance of specific interactions was noted in the early 1970s. Hydrogen bonding as a specific interaction offering the ability to yield miscibility in countless polymer blends has been well documented by Coleman and Painter and summarized in a treatise on this subject [4]. Reactive compatibilization concepts also emerged in the early 1970s [45–46], but the major research and development effort was catalyzed by the introduction of super-tough nylon 6,6 which employed reactive extrusion. The application of equation-of-state theories to polymer blends has been useful in showing qualitative trends and predicting phase

Table 1.2: Approaches for Achieving Miscible Blends or Compatible Phase Separated Blends

Miscibility	Compatibility in phase separated blends
Hydrogen bonding	Ternary component addition
Dipole-dipole interactions	Block and graft copolymer addition
Matched solubility parameters	Reactive compatibilization
Ion-dipole interactions	Cocrosslinking
Mean field approach	Interpenetrating networks
Association model	In-situ polymerization
	Nanoparticle addition

behavior such as lower critical solution temperature (*lcst*) behavior. The seminal paper by McMaster [47] prompted many further studies in this area. Spinodal decomposition as a phase separation process was noted to be possible for polymer-polymer mixtures leading to a highly interconnected morphology [48]. The recognition that intramolecular repulsion could yield a driving force towards miscibility was recognized simultaneously by three laboratories [49–51] and has been shown to be a useful method to design miscible polymer blends.

A number of useful analytical and characterization methods have been developed for polymer blends allowing for an improved understanding of the nature of miscibility and phase behavior. The use of low molecular weight analog compounds as models for high molecular weight polymers proposed initially by work at the University of Texas [52] has been particularly useful. The heat of mixing of low molecular weight liquids is easy to determine and is closely related to the expected heat of mixing of high molecular weight compounds (which cannot be directly measured). Small-angle neutron scattering (SANS) provided the evidence of mixing at the segmental level for miscible polymers thus providing the proof that indeed polymers can mix at the segmental level. This possibility was still in question three decades ago. Nuclear magnetic resonance (NMR) and fluorescence spectroscopy also yielded information on the extent of mixing and the level of miscibility achieved in specific polymer blends. Today, a number of methods exist to determine the degree of mixing at the nm scale of dimensions, as will be detailed in Chapter 5.

1.3 Overview of the Book

This book is an introduction to polymer blends as well as a reference text. Most subjects are well-covered in various reviews or book chapters and thus will not be covered in depth. Detailed theoretical discussions, such as equation of state theories, are considered beyond the scope of this book and will only be briefly discussed. In choosing the references to highlight, those references which form the basis of the polymer blend technology are emphasized along with more recent references on a specific subject. This book is not designed to be a detailed review but rather a guide to specific subject areas and the references where more comprehensive coverage can be located.

This book is divided into specific subject areas of importance to polymer blend technology starting in Chapter 2 with the fundamentals. In this chapter, the thermodynamic relationships relevant to polymer blends are detailed along with discussions on the phase behavior and phase separation processes. Specific interactions in polymer blends leading to miscibility or improved mechanical compatibility are also discussed. The mean field theory and the association model are presented. The importance of the interfacial characteristics of phase separated polymer blends is also covered in Chapter 2. In Chapter 3, compatibilization methods for achieving compatibility of phase separated blends are discussed, including the methods noted in Table 1.2.

Chapter 4 discusses the various types of polymer blends as noted in Table 1.1. The discussion of polymer blend types is highly referenced with limited detail on the discussion of specific polymer blends. Chapter 5 discusses the characterization methods commonly employed to ascertain the morphology, phase behavior and molecular interactions in polymer blends.

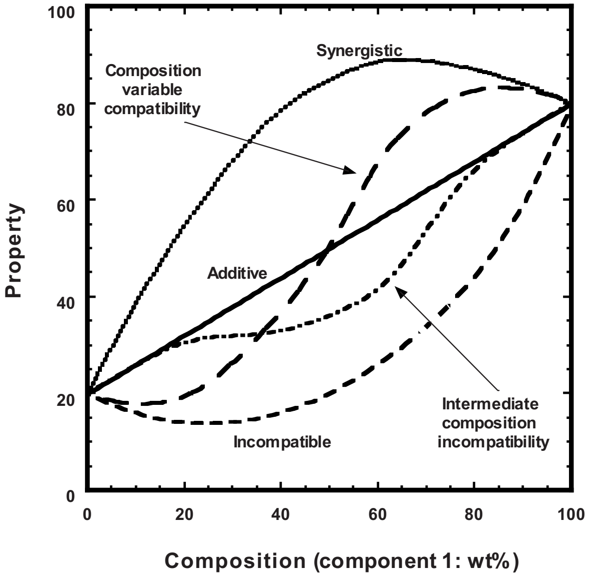

Figure 1.1: Generalized property/composition behavior of polymer blends

The properties of polymer blends (including mechanical, calorimetric, electrical, transport, rheology) are covered in Chapter 6. The property-composition relationships observed in polymer blends comprise countless possibilities including several noted in Fig. 1.1 specifically related to mechanical properties. Understanding the structure-property relationships for polymer blends is a key goal of many blend investigations and discussions in Chapter 6 will elucidate these relationships. The commercial activity of polymer blends discussed in Chapter 7 provides evidence of the importance of polymer blend technology. The emerging areas in polymer blend science and technology and future prospects of polymer blend utilization in the technologies of the future are presented in Chapter 8.

1.4 Definitions

Miscibility: Miscibility is considered to be the level (scale) of mixing of polymeric constituents of a blend yielding a material which exhibits the properties expected of a single phase material. *Note*: this does not imply or require ideal mixing, but will be expected to be mixed approaching the segmental scale of dimensions. Structure can still be expected in the 1–2 nm range and is often observed. Miscibility is established from thermodynamic relationships to be discussed later.

Immiscibility: A blend is considered immiscible if it is separated into phases comprised primarily of the individual constituents. Phase separation is also established from thermodynamic relationships.

Partial miscibility: A blend is considered partially miscible if there exists phase separation but each polymer rich phase contains a sufficient amount of the other polymer to alter the properties of that phase (e.g., the glass transition temperature).

Mechanical compatibility/compatibility: Compatibility is a general term used to imply useful properties of a polymer blend. Generally, the mechanical properties are employed as a reference to the degree of compatibility. Compatibilization of incompatible polymer blends is a major area of research and development. The degree of compatibility is generally related to the level of adhesion between the phases and the ability to transmit stress across the interface.

Microheterogeneous: A blend is described as microheterogeneous if it is comprised of a wide range of compositionally different phases. While the blend may exhibit a single glass temperature peak, it is comprised of a distribution of glass transition temperatures between the component values.

A detailed listing of the definitions of the many terms employed in polymer blends, composites and multiphase polymeric materials (IUPAC recommendation 2004) is provided in [53].

References

[1] Paul, D. R. and Newman, S. (Eds.), *Polymer Blends, Vol. 1 and 2*, (1978) Academic Press, New York

[2] Olabisi, O., Robeson, L. M. and Shaw, M. T., *Polymer-Polymer Miscibility* (1979) Academic Press, New York

[3] Utracki, L. A., *Polymer Alloys and Blends: Thermodynamics and Rheology* (1989) Hanser Publishers, New York

[4] Coleman, M. M., Graf, J. F. and Painter, P. C., *Specific Interactions and the Miscibility of Polymer Blends* (1991) Technomic Publishing Co., Inc., Lancaster

[5] Paul, D. R. and Bucknall, C. B. (Eds.), *Polymer Blends, Vol. 1 (Formulation) and Vol. 2 (Performance)*, (2000) John Wiley & Sons, New York

[6] Manson, J. A. and Sperling, L. H., *Polymer Blends and Composites* (1976) Plenum Press, New York

[7] Sperling, L. H., *Polymeric Multicomponent Materials* (1997) John Wiley & Sons, Inc., New York

[8] Miles, I. S. and Rostami, S. (Eds.), *Multicomponent Polymer Systems*, (1992) Longman Scientific and Technical, UK

[9] Folkes, M. J. and Hope, P. S. (Eds.), *Polymer Blends and Alloys*, (1993) Blackie Academic & Professional, London

[10] Shonaike, G. O. and Simon, G. P. (Eds.), *Polymer Blends and Alloys*, (1999) Marcel Dekker, New York

[11] Araki, T., Tran-Cong, Q. and Shibayama, M. (Eds.), *Structure and Properties of Multiphase Polymeric Materials*, (1998) Marcel Dekker, New York

[12] Datta, S. and Lohse, D. J., *Polymeric Compatibilizers* (1996) Hanser Publishers, New York

[13] Sperling, L. H. (Ed.), *Recent Advances in Polymer Blends, Grafts and Blocks*, (1974) Plenum Press, New York

[14] Solc, K. (Ed.), *Polymer Compatibility and Incompatibility: Principles and Practice*, (1982) MMI Press Symposium Series, Vol. 2, Harwood Academic Publishers, New York

[15] Utracki, L. A. (Ed.), *Polymer Blends Handbook: Vols. 1 and 2*, (2002) Kluwer Academic Publishers, Dordrecht

[16] Paul, D. R. and Sperling, L. H. (Eds.), *Multicomponent Polymer Materials*, (1986) Advances in Chemistry Series 211, American Chemical Society, Washington, DC

[17] Walsh, D. J., Higgins, J. S. and Maconnachie, A. (Eds.), *Polymer Blends and Mixtures*, (1985) NATO ASI Series, Series E: Applied Sciences- No. 89, Martinus Nijhoff Publishers, Dordrecht

[18] Simon, G. P. (Ed.), *Polymer Characterization Techniques and Their Application in Blends,* (2003) Oxford University Press, Oxford

[19] Klempner, D. and Frisch, K. C. (Eds.), *Polymer Alloys, Blends, Blocks, Grafts and Interpenetrating Networks,* (1977) Plenum Press, New York

[20] Klempner, D. and Frisch, K. C. (Eds.), *Polymer Alloys II, Blends, Blocks, Grafts and Interpenetrating Networks,* (1980) Plenum Press, New York

[21] Klempner, D. and Frisch, K. C. (Eds.), *Polymer Alloys III: Blends, Blocks, Grafts and Interpenetrating Networks,* (1983) Plenum Press, New York

[22] Xanthos, M. (Ed.), *Reactive Extrusion: Principles and Practice,* (1992) Hanser Publishers, Munich

[23] *Encyclopaedic Dictionary of Commercial Polymer Blends,* Utracki, L. A. (Ed.) (1994) ChemTec Publishing, Toronto

[24] Han, C. D. (Ed.), *Polymer Blends and Composites in Multiphase Systems*, (1984) Adv. Chem. Ser. 206, American Chemical Society, Washington, DC

[25] Utracki, L. A. and Weiss, R. A. (Eds.), *Multiphase Polymers: Blends and Ionomers,* (1989), ACS Symp. Ser. 395, American Chemical Society, Washington, DC

[26] Kryszewski, M., Galeski, A. and Martuscelli, E. (Eds.), *Polymer Blends: Processing, Morphological and Properties, Vol. 2*, (1984) Plenum Press, New York

[27] Culbertson, B. M. (Ed.), *Contemporary Topics in Polymer Science, Vol. 6,: Multiphase Macromolecular Systems*, (1989) Plenum Press, New York

[28] Lipatov, Y. S. and Nesterov, A. E., *Thermodynamics of Polymer Blends* (1997) Technomic, Lancaster

[29] Utracki, L. A., *Commercial Polymer Blends* (1998) Chapman and Hall, London

[30] Baker, W., Scott, C. and Hu, G.-H. (Eds.), *Reactive Polymer Blending*, (2001) Hanser Publishers, Munich

[31] Platzer, N. A. J. (Ed.) *Copolymers, Polyblends and Composites*, 1975 American Chemical Society, Washington, D. C.

[32] Ottenbrite, R. M., Utracki, L. A. and Inoue, S. (Eds), *Current Topics in Polymer Science, Vol. II: Rheology and Polymer Processing/Multiphase Systems*, (1987) Hanser, Munich

[33] Sperling, L. H., *Interpenetrating Polymer Networks and Related Materials* (1981) Plenum Press, New York

[34] Klempner, D., Sperling, L. H. and Utracki, L. A. (Eds.), *Interpenetrating Polymer Networks,* (1994) Adv. Chem. Ser. 239, American Chemical Society, Washington, DC

[35] Kim, S. C. and Sperling, L. H. (Eds.), *IPNs Around the World: Science and Engineering,* (1997) John Wiley & Sons, New York

[36] Riew, C. K. and Kinloch, A. J. (Eds.), *Toughened Plastics I: Science and Engineering,* (1993) Adv. Chem Ser. 233, American Chemical Society, Washington, DC

[37] Riew, C. K. and Kinloch, A. J. (Eds.), *Toughened Plastics II: Novel Approaches in Science and Engineering*, (1996) Adv. Chem Ser. 252, American Chemical Society, Washington, DC

[38] Arends, C. B. (Ed), *Polymer Toughening,* (1996) Marcel Dekker, New York

[39] Aylsworth, J. W., U. S. Patent 1 111 284 (1914); also see Sperling, L. H., *Polym. News* (1987) 12, p. 332

[40] Badum, E., U. S. Patent 2 297 194 (1942)

[41] Henderson, D. E., U. S. Patent 2 330 353 (1943)

[42] Zakrzewski, G. A., *Polymer* (1973) 14, p. 348

[43] Wagner, E. R., Robeson, L. M., *Rubber Chem Technol.* (1970) 43, p. 1129

[44] Shultz, A. R. and Beach, B. M., *Macromolecules* (1974) 7, p. 902

[45] McGrath, J. E., Robeson, L. M. and Matzner, M., In *Recent Advances in Polymer Blends*, *Grafts and Blocks*, Sperling, L. H. (Ed), (1974) Plenum Press, New York, p. 195; also *Polym. Prepr*. (1973) 14(2), p. 1032

[46] Ide, F. and Hasegawa, A., *J. Appl. Polym. Sci.* (1974) 18, p. 963

[47] McMaster, L. P., *Macromolecules* (1973) 6, p. 760

[48] McMaster, L. P., In *Copolymers, Polyblends and Composites*: Adv. Chem. Ser. 142, Platzer, N. A. J. (Ed), (1975) American Chemical Society, Washington, D. C., p. 43

[49] tenBrinke, G., Karasz, F. E. and MacKnight, W. J., *Macromolecules* (1983) 16, p. 1827

[50] Kambour, R. P., Bendler, J. T. and Bopp, R. C., *Macromolecules* (1983) 16, p. 753

[51] Paul, D. R. and Barlow, J. W., *Polym*. (1984) 25, p. 487

[52] Cruz, C. A., Barlow, J. W. and Paul, D. R., *Macromolecules* (1979) 112, p. 726

[53] Work, W. J., Horie, K., Hess, M. and Stepto, R. F. T., *Pure Appl. Chem*. (2004) 76, p. 1985

2 Fundamentals of Polymer Blends

2.1 Thermodynamic Relationships

The most important characteristic of a polymer blend of two (or more) polymers is the phase behavior. Polymer blends (like low molecular weight solvents) can exhibit miscibility or phase separation and various levels of mixing in between the extremes (e.g., partial miscibility). The most important factor leading to miscibility in low molecular weight materials is the combinatorial entropy contribution which is very large compared to high molecular weight polymers. This contribution is the reason that solvent-solvent mixtures offer a much broader range of miscibility than polymer-solvent combinations. The range of miscible combinations involving polymer-polymer mixtures is even much smaller. As an example compare the miscibility of hexane-ethanol mixtures with their high molecular weight analogs of polyolefins and poly(vinyl alcohol). The former is miscible. whereas the latter is highly immiscible. This is well-demonstrated by the following discussion.

The most important relationship governing mixtures of dissimilar components 1 and 2 is:

$$\Delta G_m = \Delta H_m - T\Delta S_m \tag{2.1}$$

where ΔG_m is the free energy of mixing, ΔH_m is the enthalpy of mixing (heat of mixing) and ΔS_m is the entropy of mixing. For miscibility to occur, ΔG_m must be smaller than 0. While this is a necessary requirement, it is not a sufficient requirement as the following expression must also be satisfied:

$$\left(\frac{\partial^2 \Delta G_m}{\partial \phi_i^2}\right)_{T,P} > 0 \tag{2.2}$$

Negative values of Eq. 2.2 (even though $\Delta G_m < 0$) can yield an area of the phase diagram where the mixture will separate into a phase rich in component 1 and a phase rich in component 2.

For low molecular weight materials, increasing temperature generally leads to increasing miscibility as the $T\Delta S_m$ term increases, thus driving ΔG_m to more negative values. For higher molecular weight components, the $T\Delta S_m$ term is small and other factors (such as non-combinatorial entropy contributions and temperature dependant ΔH_m values) can dominate and lead to the reverse behavior, namely, decreasing miscibility with increasing temperature.

Thus, while liquid-liquid and polymer-solvent mixtures (that are borderline in miscibility) usually exhibit upper critical solution temperatures (*ucst*), polymer-polymer mixtures generally exhibit lower critical solution temperatures (*lcst*). This behavior is illustrated in Fig. 2.1 with an illustration of the free energy composition at key temperatures noted in Fig. 2.2. The binodal and spinodal curves (binodal and spinodal phase separation processes are discussed later in this chapter) are illustrated on the phase diagrams. The spinodal curve is related to the position where

$$\left(\frac{\partial^2 \Delta G_m}{\partial \phi_i^2}\right)_{T,P} = 0 \tag{2.3}$$

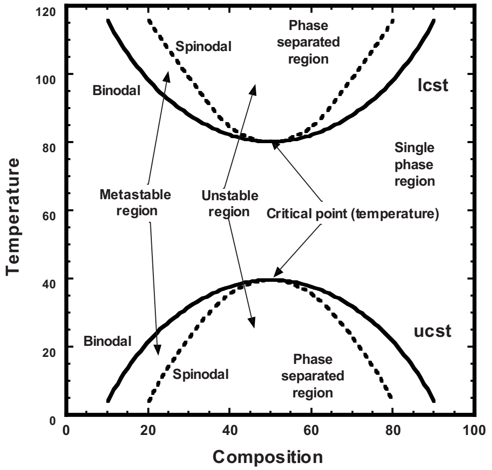

Figure 2.1: Phase diagram showing *lcst* and *ucst* behavior for polymer blends

The binodal curve is related to the equilibrium phase boundary between the single phase and the phase separated region. In a binary system, this is related to the chemical potentials of an individual component being equal in both phases as expressed by the following relationships:

$$\Delta\mu_1^a = \Delta\mu_1^b \qquad \Delta\mu_2^a = \Delta\mu_2^b \tag{2.4}$$

where 1,2 represent the two polymers and a,b represent the phases. The chemical potential is defined as the rate of change of the Gibbs function of the system with respect to the change in the number of moles of a specific component. The values of the binodal curve can be determined from the double tangent to the ΔG_m curve shown in Fig. 2.2, as noted by Koningsveld [1]. The critical point, where the binodal and spinodal intersect, is determined from the expression:

$$\left(\frac{\partial^3 \Delta G_m}{\partial \phi^3}\right)_{T,P} = 0 \tag{2.5}$$

The experimental phase diagrams are often not symmetrical, unless the molecular weights of the components are similar, and in the case of large differences in molecular weights, they can be highly non-symmetric. With phase separation, the binodal defines the composition of the component 1 rich phase and component 2 rich phase. The tie line noting temperature T_2 between the binodal points can be employed to determine the relative amounts of each phase. The tie line is illustrated in Fig. 2.3. The volume fraction of component 1 rich phase, ϕ_{1r}, and component 2 rich phase, ϕ_{2r}, can be determined from the expression, with ϕ representing the overall composition of the component noted in Fig. 2.3:

$$\frac{\phi_{1r}}{\phi_{2r}} = \frac{\phi_b - \phi}{\phi - \phi_a} \tag{2.6}$$

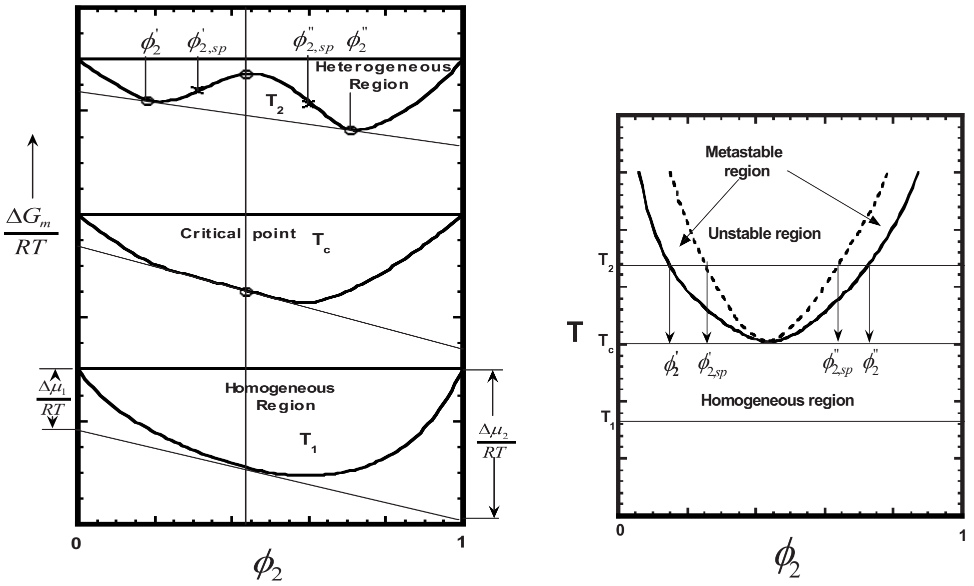

Figure 2.2: Free energy of mixing versus volume fraction generalized behavior for various positions on the phase diagram

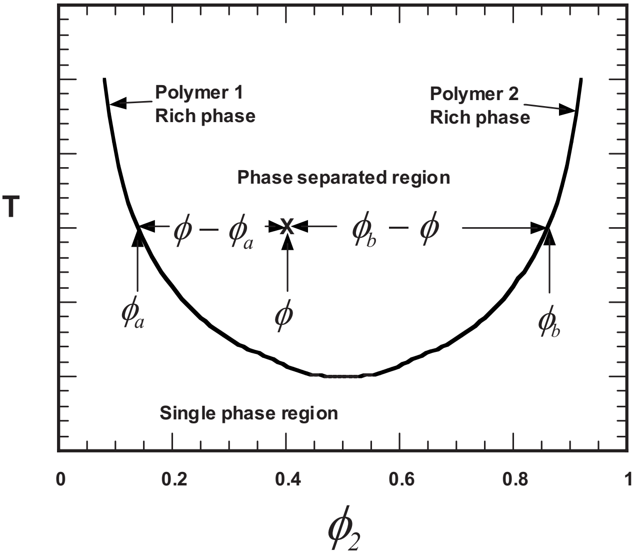

Figure 2.3: Tie-line calculation of phase compositions

Highly miscible polymers exhibit single phase behavior over the entire temperature-volume fraction space available for experimental verification. If *ucst* or *lcst* behavior exists, it cannot be determined. At low temperatures, the *ucst* cannot be determined due to the glassy state restricting molecular motion (phase separation); and at higher temperatures, polymer degradation occurs before phase separation can be observed. With highly immiscible polymer blends, the phase diagram is virtually all in the two phase region with the binodal curves virtually overlapping the y axis at 0 and 1.0 volume fraction.

2.1.1 Combinatorial Entropy of Mixing

The entropy of mixing for mixtures of dissimilar components is an important contribution to the ability to achieve miscibility. The determination of the entropy of mixing begins with the Boltzmann relationship:

$$\Delta S_m = k \ln \Omega \tag{2.7}$$

where Ω represent the summation of combinations of arranging N_1 and N_2 molecules into a regular lattice of N ($N = N_1 + N_2$) cells.

$$\Omega = \frac{N!}{N_1! N_2!} \tag{2.8}$$

and application of Sterling's approximation yields:

$$\ln N! = N \ln N - N \tag{2.9}$$

Substitution of Eq. 2.9 into Eq. 2.8 and then Eq. 2.7 yields:

$$\Delta S_m = k(N \ln N - N_1 \ln N_1 - N_2 \ln N_2) = -k(N_1 \ln x_1 + N_2 \ln x_2) \tag{2.10}$$

where $x_1 = N_1/N$ and $x_2 = N_2/N$. This equation is valid for equal sized low molecular weight molecules. For a mixture of solvent and polymer it was recognized that the above expression did not agree with experimental observations. Specifically for solvent (1), the term $N_1 \ln x_1 \gg N_2 \ln x_2$, and thus predicted that the presence of polymer would exhibit no change in the free energy of mixing as both the enthalpy and entropy would be dominated by the mole fraction, x_1, which would be $\sim$1 except in extremely low concentrations of solvent in the polymer. Vapor pressure measurements among other colligative property determinations showed that the free energy of mixing is changed and the value of mole fraction was replaced with volume fraction, ϕ_i, to yield more realistic agreement.

For polymers, the assumption is made that the lattice is comprised of N cells with a volume of V. Each polymer molecule occupies volumes V_1 and V_2, respectively, with each mer unit occupying a volume, V_{mer}. The molecular volume, V_i, is equal to the product of V_{mer} and the number of mer units. For solvents, the number of mer units is 1. The volume fractions ϕ_1 and ϕ_2 are represented by the equations:

$$\phi_1 = \frac{V_1 N_1}{V_1 N_1 + V_2 N_2}; \quad \phi_2 = \frac{V_2 N_2}{V_1 N_1 + V_2 N_2} \quad \text{and} \quad V = V_1 N_1 + V_2 N_2 \tag{2.11}$$

With the assumptions noted above for placement of polymers in the lattice, the substitution of the assumptions into Eq. 2.11 and Eq. 2.10 leads to:

$$\Delta S_m = -k(N_1 \ln \phi_1 + N_2 \ln \phi_2) = -kV\left[\frac{\phi_1}{V_1}\ln\phi_1 + \frac{\phi_2}{V_2}\ln\phi_2\right] \text{ or}$$
$$\Delta S_m = -RV\left(\frac{\phi_1}{v_1}\ln\phi_1 + \frac{\phi_2}{v_2}\ln\phi_2\right) \tag{2.12}$$

for molecular volume or molar volume, respectively. Note that the change from mole fraction to volume fraction for x_1 and x_2 is valid if it is assumed that this ratio is expressed as the number of cells occupied by segments of 1 (or 2) over the total number of cells in the lattice. The one basic problem with this approach is the selection of the mer units such that the mer units of the different polymers occupy a similar volume. As with many theories, this approach is not ideal however, it allows for at least a qualitative assessment of the thermodynamics of polymer blends. The lattice arrangements for solvent-solvent, solvent-polymer and polymer-polymer combinations are illustrated in Fig. 2.4, demonstrating the combinations of arranging the molecules follows: solvent-solvent $\gg$ solvent-polymer $\gg$ polymer-polymer.

The combinatorial entropy of mixing (Eq. 2.12) is thus established for the Flory-Huggins theory which follows. As the ln ϕ_i value is negative, ΔS_m is positive and the expression ($-T\Delta S_m$) in Eq. 2.1 leads to a negative contribution to ΔG_m, thus improving the potential for miscibility. As noted with high molecular weight polymers, this contribution becomes negligible. A discussion of the lattice approach and derivation of the entropy of mixing can be found in [2].

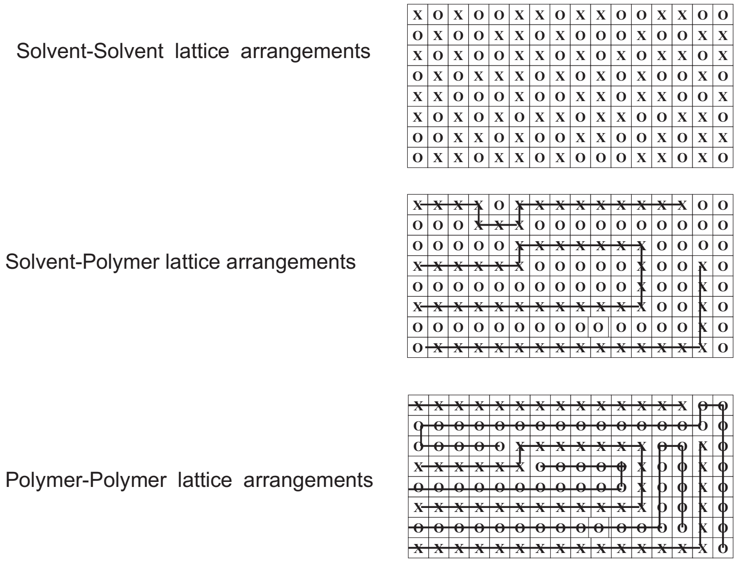

Figure 2.4: Schematic of solvent-solvent, solvent-polymer and polymer-polymer arrangements in a lattice of N cells; visual illustration of combinatorial entropy

2.1.2 Enthalpy of Mixing

The enthalpy (heat) of mixing expression for Eq. 2.1 is derived from the relationship:

$$w_{12} = \frac{1}{2}(\varepsilon_{11} + \varepsilon_{22}) - \varepsilon_{12} \tag{2.13}$$

where ε_{ij} is the energy of contacts between components i and j and w_{12} is the exchange energy of interacting segments. The heat of mixing is related to w_{12} by the expression:

$$\frac{\Delta H_m}{V} = \frac{z w_{12}}{v_r} \phi_1 \phi_2 \tag{2.14}$$

where z is the coordination number (generally assumed as 8, but in the range of 6 to 12), υ_r is the interacting segment volume and is often referred to as the reference volume. In this discussion, υ_r can represent molecular or molar segment volumes, depending on whether molecular or molar parameters are employed in the analysis with the difference being the magnitude of the difference between k and R (Boltzmann's constant and the gas constant). A parameter termed the Flory-Huggins interaction parameter, χ_{12}, has been typically employed, defined as:

$$\chi_{12} = \frac{z w_{12}}{kT} \qquad \text{or} \qquad \chi_{12} = \frac{z w_{12}}{RT} \text{ (for molar parameters)} \tag{2.15}$$

leading to

$$\Delta H_m = \phi_1 \phi_2 RTV \frac{\chi_{12}}{v_r} \tag{2.16}$$

For dispersive and non-polar (or modest polar) interactions, ε_{12} can be estimated by a geometric mean:

$$\varepsilon_{12} = (\varepsilon_{11}\varepsilon_{22})^{1/2} \qquad \text{yielding} \quad w_{12} = \frac{1}{2}\left(\varepsilon_{11}^{1/2} - \varepsilon_{22}^{1/2}\right)^2 \tag{2.17}$$

This leads to solubility parameter concepts (discussed later in this chapter), used by Hildebrand [3] to show that:

$$z\left(\varepsilon_{11}^{1/2} - \varepsilon_{22}^{1/2}\right)^2 \Big/ 2v_r = (\delta_1 - \delta_2)^2 \tag{2.18}$$

Thus,

$$(\delta_1 - \delta_2)^2 = z w_{12} / \upsilon_r = \chi_{12} RT / v_r \qquad \text{and} \qquad \frac{\Delta H_m}{V} = (\delta_1 - \delta_2)^2 \phi_1 \phi_2 \tag{2.19}$$

where δ_i is the solubility parameter for component i (defined later in the chapter).

A discussion of the enthalpy of mixing and derivation of the above relationships can be found in [2, 3].

2.1.3 Flory-Huggins Theory

The most relevant theory for modeling the free energy of binary polymer mixtures is the Flory-Huggins theory, initially employed for solvent-solvent and polymer-solvent mixtures. This theory was independently derived by Flory [4, 5] and Huggins [6, 7]. The key equation (combined from discussions earlier in this chapter on entropy and enthalpy of mixing) is:

$$\Delta G_m = kTV\left[\frac{\phi_1}{V_1}\ln\phi_1 + \frac{\phi_2}{V_2}\ln\phi_2\right] + \phi_1\phi_2\chi_{12}\ kTV\big/\,v_r \quad \text{(molecular basis)} \tag{2.20a}$$

$$\Delta G_m = RTV\left[\frac{\phi_1}{v_1}\ln\phi_1 + \frac{\phi_2}{v_2}\ln\phi_2\right] + \phi_1\phi_2\chi_{12}\ RTV\big/\,v_r \quad \text{(molar basis)} \tag{2.20b}$$

where V = total volume, R = gas constant, ϕ_i = volume fraction of component i, V_i= molecular volume, υ_i = molar volume of polymer chain i, υ_r = molecular or molar volume of a specific segment (depending on whether Eq. 2.20a or 2.20b is employed), χ_{12} = Flory-Huggins interaction parameter and k is the Boltzmann's constant. υ_r is often calculated as the square root of the product of the individual segmental unit molecular or molar volumes of the polymeric components ($v_r = \sqrt{v_1 v_2}$). χ'_{12} is further simplified to χ_{12} (binary interaction parameter), defined as $\chi'_{12} = \chi_{12}/\upsilon_r$ and often as a binary interaction density parameter, B, defined as $B = \chi'_{12}RT$. As the use of χ_{12} and χ'_{12} is often interchanged in the literature, some confusion may exist. The following discussion will employ the molar basis (Eq. 2.20b). From Eq. 2.12, it is apparent that the term in Eq. 2.20b:

$$RTV\left[\frac{\phi_1}{v_1}\ln\phi_1 + \frac{\phi_2}{v_2}\ln\phi_2\right] = -T\Delta S_m \tag{2.21}$$

Thus, from the relationship, $\Delta G_m = \Delta H_m - T\Delta S_m$, then

$$\Delta H_m = \phi_1\phi_2\chi_{12}RTV/v_r = \phi_1\phi_2 B_{12}V \tag{2.22}$$

As $v_i = M_i/\rho_i$; the following expression is also commonly utilized:

$$\Delta G_m = RTV\left[\frac{\rho_1\phi_1}{M_1}\ln\varphi_1 + \frac{\rho_2\phi_2}{M_2}\ln\phi_2\right] + B_{12}\phi_1\phi_2V \tag{2.23}$$

where M_i = molecular weight of component i and ρ_i = density of component i. For simplicity, the volume is divided into both sides of the equation and some references also assume $\rho_1 = \rho_2 = \rho$; allowing further simplification yielding the expression

$$\frac{\Delta G_m}{V} = \rho RT\left[\frac{\phi_1}{M_1}\ln\phi_1 + \frac{\phi_2}{M_2}\ln\phi_2\right] + B_{12}\phi_1\phi_2 \tag{2.24}$$

In some references, ΔG_m is expressed as the term $\Delta G_m/V$ in Eq. 2.24, in those cases ΔG_m has units of cal/cc. Unless noted otherwise, ΔG_m in this text has units of cal. Also, in some cases, ρ is assumed to equal 1.0 g/cc and is eliminated from the equation; however, the units remain and must be accounted for.