Lloyd M. Robeson

# **Polymer Blends**

# A Comprehensive Review



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# 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

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# 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

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

#### Table 1.1: Types of Polymer Blends

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 improve 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<sup>®</sup>. 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 supertough 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

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

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

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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].

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## 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  $\Delta G_m$  is the free energy of mixing,  $\Delta H_m$  is the enthalpy of mixing (heat of mixing) and  $\Delta S_m$  is the entropy of mixing. For miscibility to occur,  $\Delta G_m$  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  $\Delta G_m$  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  $\Delta H_m$  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  $\Delta G_m$  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,  $\phi_{1r}$ , and component 2 rich phase,  $\phi_{2r}$ , can be determined from the expression, with  $\phi$  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  $\Omega$  represent the summation of combinations of arranging N<sub>1</sub> and N<sub>2</sub> molecules into a regular lattice of N (N = N<sub>1</sub>+ N<sub>2</sub>) 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:

$$\Delta S_m = k(N \ln N - N_1 \ln N_1 - N_2 \ln N_2) = -k(N_1 \ln x_1 + N_2 \ln x_2)$$
(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,  $\phi_i$ , 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  $\phi_1$  and  $\phi_2$  are represented by the equations:

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

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

$$\Delta S_m = -RV \left( \frac{\phi_1}{\nu_1} \ln \phi_1 + \frac{\phi_2}{\nu_2} \ln \phi_2 \right)$$
(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 polymerpolymer 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  $\phi_i$  value is negative,  $\Delta S_m$  is positive and the expression  $(-T\Delta S_m)$  in Eq. 2.1 leads to a negative contribution to  $\Delta G_m$ , 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].

	X	0	X	0	0	X	х	0	х	х	0	0	X	х	0	0
			0	0	х	х	0	X	0	0	0	X	0	0	X	X
Solvent-Solvent lattice arrangements	X	0	х	0	0	х	х	0	х	0	х	0	х	х	0	X
	0	х	0	х	х	х	0	х	0	х	0	X	0	0	X	0
	X	х	0	0	0	х	0	0	х	х	0	х	х	0	0	X
	X	0	х	0	х	0	х	х	0	х	X	0	0	х	X	0
	0	0	х	х	0	х	0	0	х	х	0	0	х	0	X	x
	0	х	х	0	х	х	0	X	0	0	0	x	х	0	X	0
	v	v	v	v	0	v	v	v	v	v	v	v	v	v		
	A-	A 0	A 0	1	U	1	A 0	A .	0	0						
	0	0	0	X O	A	X	0	0	0	0	0	0	0	0		0
Solvent-Polymer lattice arrangements	0	0	0	0	0	1	A	A	A	A	A	1	0	0	U	0
	X	A	Ä	Ā	Ä	X	0	0	0	0	0	1	0	0	£	0
	0	0	0	0	0	0	0	0	0	0	0	X	0	0	K	0
	X	X	X	X	X	X	X	X	X	X	X	X	0	0	K	0
	0	0	0	0	0	0	0	0	0	0	0	0	0	0	×	0
	0	х	X	х	X	X	х	X	х	х	X	х	X	X	-X	0
	X	X	X	X	X	X	X	X	X	X	X	X	X	×	P	Ψ
	9	0	0	0	0	0	0	0	0	0	0	0	0	0	-0	•
	0	0	0	0	÷	1¥	X	X	X	X	X	٦¥	P	P	<b>K</b>	φ
Polymor Polymor lattice arrangements		х	X	х	х	X	0	0	0	0	1	X	ρ	•	ĸ	•
i orymer orymer rattice arrangements			0	0	0	0	0	0	0	0	ø	X	ρ	Ø	ĸ	0
	X	X	X	х	X	X	х	X	X	X	X	×	ρ	Ø	K	0
	•	0	0	0	0	0	0	0	0	0	0	0	ю	Q	ĸ	Ø
	X	X	X	X	х	X	Х	X	х	X	X	X	X	X	-X	Ø

**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:

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

where  $\varepsilon_{ij}$  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),  $v_r$  is the interacting segment volume and is often referred to as the reference volume. In this discussion,  $v_r$  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,  $\chi_{12}$ , has been typically employed, defined as:

$$\chi_{12} = \frac{zw_{12}}{kT}$$
 or  $\chi_{12} = \frac{zw_{12}}{RT}$  (for molar parameters) (2.15)

leading to

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

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

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

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

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

Thus,

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

where  $\delta_i$  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:

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

$$\Delta G_m = RTV \left[ \frac{\phi_1}{\nu_1} \ln \phi_1 + \frac{\phi_2}{\nu_2} \ln \phi_2 \right] + \phi_1 \phi_2 \chi_{12} RTV / \nu_r \quad (\text{molar basis})$$
(2.20b)

where V = total volume, R = gas constant,  $\phi_i =$  volume fraction of component i,  $V_i$ = molecular volume,  $v_i =$  molar volume of polymer chain i,  $v_r =$  molecular or molar volume of a specific segment (depending on whether Eq. 2.20a or 2.20b is employed),  $\chi_{12} =$  Flory-Huggins interaction parameter and k is the Boltzmann's constant.  $v_r$  is often calculated as the square root of the product of the individual segmental unit molecular or molar volumes of the polymeric components ( $v_r = \sqrt{v_1 v_2}$ ).  $\chi'_{12}$  is further simplified to  $\chi_{12}$  (binary interaction parameter), defined as  $\chi'_{12} = \chi_{12}/v_r$  and often as a binary interaction density parameter, B, defined as  $B = \chi'_{12}RT$ . As the use of  $\chi_{12}$  and  $\chi'_{12}$  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:

$$RTV\left[\frac{\phi_1}{\nu_1}\ln\phi_1 + \frac{\phi_2}{\nu_2}\ln\phi_2\right] = -T\Delta S_m$$
(2.21)

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

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

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

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

where  $M_i$  = molecular weight of component i and  $\rho_i$  = 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

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

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

The critical values for achieving miscibility are defined by Eqs. 2.3 and 2.5:

$$\chi_{12,cr}' = \frac{B_{12,cr}}{RT_{cr}} = \frac{1}{2} \left[ \frac{1}{\nu_1^{1/2}} + \frac{1}{\nu_2^{1/2}} \right]^2 \quad \text{and} \quad \phi_{cr} = \frac{\nu_1^{1/2}}{\nu_1^{1/2} + \nu_2^{1/2}}$$
(2.25)

or in terms of molecular weight (assuming density of the polymers is equal)

$$\chi_{12,cr}' = \frac{B_{12,cr}}{RT_{cr}} = \frac{1}{2} \rho \left[ \frac{1}{M_1^{1/2}} + \frac{1}{M_2^{1/2}} \right]^2 \quad \text{and} \quad \phi_{cr} = \frac{M_1^{1/2}}{M_1^{1/2} + M_2^{1/2}}$$
(2.26)

The miscibility region is therefore defined by the relationship

$$\chi_{12}' \text{ or } \frac{B_{12}}{RT} < \frac{1}{2} \left[ \frac{1}{v_1^{1/2}} + \frac{1}{v_2^{1/2}} \right]^2 \quad \text{or} \quad \chi_{12}' \text{ or } \frac{B_{12}}{RT} < \frac{1}{2} \rho \left[ \frac{1}{M_1^{1/2}} + \frac{1}{M_2^{1/2}} \right]^2$$
 (2.27)

As the molecular weights of the respective polymers increase,  $\chi'_{12,cr}$  and  $B_{12,cr} \rightarrow 0$ . Often, the density of both polymers is assumed = 1.0 g/cc, and  $\rho$  is eliminated from the equations (again units must be accounted for). With  $\rho = 1.0$  g/cc and equal molecular weight for the components,  $\chi'_{12,cr} = 2/M$  mole/cc and  $B_{12} = 2RT/M$  cal/cc.

For the spinodal condition (Eq. 2.3) to be satisfied, the second derivative of Eq. 2.23 yields:

$$\left(\frac{\partial^2 \Delta G_m}{\partial \phi_i^2}\right)_{T,p} = 0 = RTV \left(\frac{\rho_1}{\phi_1 M_1} + \frac{\rho_2}{\phi_2 M_2}\right) - 2B_{12}V$$
(2.28)

The first part of Eq. 2.20 (a and b) is the combinatorial entropy of mixing. As the molecular weight of component 1 and/or 2 increases, the negative value inherent with this expression becomes vanishingly small. For solvent-solvent and polymer-solvent mixtures, the combinatorial entropy of mixing is finite and an important contribution to the free energy of mixing. For such mixtures, strong positive values of the interaction density, *B*, will be required to yield phase separation. With high molecular weight polymers, the enthalpy of mixing term  $(B_{12}\phi_1\phi_2 V)$  determines the phase behavior of the polymer blend. As the magnitude and sign (positive or negative) of  $B_{12}$  is related to  $w_{12}$ , Eq. 2.13 illustrates the importance of interaction energies between unlike components compared to the averaged values of the like components of the mixture.

The combinatorial entropy term is multiplied by temperature, thus illustrating improved miscibility with increasing temperature as is typically observed with solvent-solvent and polymer-solvent mixtures. With high molecular weight polymers, this term is very small, thus increasing temperature will have no significant effect. Heat of mixing experiments have shown a strong temperature dependence in cases of specific interactions (e.g., hydrogen bonding). These studies [8, 9] show an increasing (from negative to positive) heat of mixing or  $\chi_{12}$  with increasing temperature, implying that the value of  $\varepsilon_{12}$  is temperature dependant. In order to provide clarity, it needs to be pointed out that negative values of  $w_{12}$ ,  $\chi'_{12}$ , and  $B_{12}$  are related to exothermic heats of mixing. It may seem confusing, but positive values for  $\Delta H_m$  indicate an endothermic heat of mixing leading to immiscibility. Negative values of  $\Delta H_m$ ,  $\chi'_{12}$ , and  $B_{12}$ 

for polymer-polymer mixtures invariably lead to single phase, miscible blends as the entropic contribution for the Flory-Huggins equation is always negative (assuming the expression in Eq. 2.2 is also satisfied). *The usual convention employed for polymer blends and utilized in this book is that a negative heat of mixing is exothermic and a positive heat of mixing is endothermic.* Other factors including non-combinatorial entropy of mixing terms not covered by the Flory-Huggins equation can also play a significant factor in the observed phase behavior as will be discussed briefly in the section on equation of state theories.

The Flory-Huggins approach is not directly capable of predicting *lcst* behavior unless a temperature dependent  $\chi_{12}$  value exhibiting increasing values (negative to positive) with increasing temperature is employed. The temperature dependence of  $\chi_{12}$  has often been expressed by  $\chi_{12} = a + (b/T)$ . For polymer-solvent mixtures,  $\chi_{12}$  has been expressed as a function of both temperature and concentration:  $\chi_{12} = a + (b/T) + c\phi_1 + d\phi_1^2$  [10].

#### 2.1.4 Equation of State Theories

An equation of state (EOS) is basically a mathematical relationship between pressure, temperature and volume. There are many equation of state relationships employed for gases (e.g., van der Waals equation, Redlich-Kwong equation of state) as noted in the seminal book by Reid, Prausnitz and Sherwood [11]. Equation of state approaches can be applied to liquids and also polymeric systems.

The Flory-Huggins approach noted above is based on analysis of a lattice model of mixture components. This approach as an incompressible model does not allow for volume changes upon mixing, and additional entropic contributions as well as enthalpic contributions will exist for mixtures with non-additive volume-composition behavior. Equation of state models developed by Prigogine [12] for liquid mixtures in the 1950s have been applied to polymersolvent solutions by Flory et al. in the 1960s [13]. Reduced variables of volume, temperature and pressure are employed for an equation of state from which the thermodynamic relationships are applied to determine the free energy of mixing, the binodal and spinodal curves, the critical points and thus the phase behavior. The specific equation of state and additivity rules allow for different equation of state approaches. While the equation of state theories offer improved quantitative information on the phase behavior of polymer mixtures, they are considerably more complex and require extensive work to compare theory with experimental results. The basis of the equation of state approach starts with the relationship:  $(\partial \mu_i / \partial P) = v_i$ , where  $v_i$ is the partial molar volume of component i and  $\mu_i$  is the chemical potential of component i. Thus, the PVT relationships for polymers can be related to the phase behavior as exemplified in the following discussion.

The Flory equation of state approach has been shown to be quite applicable to polymer mixtures (see McMaster [14]). The Flory equation of state approach involved the characterization of components by three parameters:  $v^*$  (the characteristic volume),  $T^*$  (the characteristic temperature) and P<sup>\*</sup> (the characteristic pressure). Reduced variables are defined as:

$$\tilde{\nu} = \nu/\nu^* \quad \tilde{P} = P/P^* \quad \tilde{T} = T/T^* \tag{2.29}$$

The volume,  $v^*$ , is the hard core volume of a polymer segment and v is the actual volume of the segment. The reduced volume,  $\tilde{v}$ , is then the reduced volume per segment.  $v^*$ ,  $\tilde{v}$ , and v are expressed as molar quantities in this discussion.

The corresponding equation of state (derivation given by Flory [13]) is:

$$\tilde{P}_{i}\tilde{\nu}_{i}/\tilde{T}_{i} = \tilde{\nu}_{i}^{1/3}/(\tilde{\nu}_{i}^{1/3} - 1) - 1/\tilde{\nu}_{i}\tilde{T}_{i}$$
(2.30)

The key parameters of  $\tilde{v}$  and  $\tilde{P}$  can be determined from the thermal expansion coefficient,  $\alpha$ , and the thermal pressure coefficient,  $\gamma$ 

$$\boldsymbol{\alpha} = (1/V)(\partial V/\partial T)_{P,N_i} \tag{2.31}$$

$$\tilde{\nu}^{1/3} = (3 + 4\alpha T)/(3 + 3\alpha T) \tag{2.32}$$

$$\gamma = (\partial P / \partial T)_{V,N_i}$$
 and  $P^* = \gamma T \tilde{\nu}^2$  (2.33)

 $T^*$  is determined at the limit of zero pressure yielding:

$$T^* = T\left\{\tilde{\nu}^{4/3}/(\tilde{\nu}^{1/3} - 1)\right\}$$
(2.34)

A constant interaction term  $X_{12}$  (similar to a binary interaction parameter) is defined and related by

$$P^* = \phi_1 P_1^* + \phi_2 P_2^* - \phi_1 \theta_2 X_{12}$$
(2.35)

 $\phi_i$  = volume fraction of component *i* based on hard core volume;  $\theta_2$  = segment surface fraction.  $X_{12}$  is related to  $\chi_{12}$  as shown by Patterson and Robard [15]

$$\frac{\chi_{12}}{M_1 \tilde{\nu}_{1sp}} = \frac{P_1^*}{RT_1^*} \left[ \frac{\tilde{\nu}_1^{1/3} X_{12}}{(\tilde{\nu}_1^{1/3} - 1)P_1^*} \right] + \left[ \frac{\tilde{\nu}_1^{1/3}}{2(4/3 - \tilde{\nu}_1^{1/3})} \right] \left[ \left( 1 - \frac{T_1^*}{T_2^*} \right)^2 \right]$$
(2.36)

The mixing relationship is defined as:

$$\phi_1 = m_1 v_{1sp}^* / (m_1 v_{1sp}^* + m_2 v_{2sp}^*)$$
(2.37)

 $\phi_2 = 1 - \phi_1$ ;  $m_i$  = mass of component I, where  $v_{isp}^*$  is based on hard core volume per unit mass (e.g., gram). The enthalpy change on mixing is equal to [16]:

$$\Delta H_m = \left(m_1 v_{1sp}^* + m_2 v_{2sp}^*\right) \left\{ \left(\phi_1 P_1^* \tilde{v}_1\right) + \left(\phi_2 P_2^* / \tilde{v}_2\right) - \left(P^* / \tilde{v}\right) \right\}$$
(2.38)

The determination of the free energy of mixing and the resultant binodal and spinodal curves (phase diagram) employing this approach has been detailed in various papers and reviews and is too complex to repeat here. These solutions were obtained from the expression

$$\Delta G_m = -kT \ln \left(\frac{Z}{\prod_{i=1}^n Z_i}\right) \text{ where } Z_i(Z_i) \text{ is obtained from } Z = (Q) \left(\frac{2\pi m_i kT}{h^2}\right)^{3N_i c_i r_i/2}$$
(2.39)

where

$$Q = \Omega_{comb} (\gamma v_i^*)^{N_i c_i r_i} (v_i^{1/3} - 1)^{3N_i c_i r_i} \exp(U_{oi} / kT)$$
(2.40)

and  $\gamma$  is the geometric factor, 3c is the number of external degrees of freedom for one segment,  $r_i$ , is the number of segments per chain. The origin of these equations and the formalism for their application to equation of state thermodynamics is noted in references [11–14, 17]. The binodal and spinodal relationships derived from this approach are complex relationships, expressed as a function of the many variables (e.g.,  $P^*$ ,  $T^*$ ,  $v^*$ ,  $v^{1/3}$ ,  $X_{12}$ ,  $Q_{12}$ ,  $\theta_i$ )), some of which are determined from PVT data and others comprising adjustable parameters.  $Q_{12}$  is related to additional entropy contributions of which one situation is a loss in entropy due to non-random mixing resulting from specific interactions.

$$\frac{\Delta G_m}{kT} = \sum_{i=1}^n N_i \ln \psi_i + \sum_{i=1}^n 3r_i N_i (c_i - c) \ln[(2\pi m_i kT)^{1/2}/h] 
+ 3\overline{r} N \sum_{j=2}^n \sum_{i=1}^{j-1} \psi_i \psi_j c_{ij} \ln \left[ (\gamma v^*)^{1/3} (\tilde{v}^{1/3} - 1) \right] + 3 \sum_{i=1}^n r_i N_i c_i \ln \left[ \frac{\tilde{v}_i^{1/3} - 1}{\tilde{v}^{1/3} - 1} \right] 
+ \frac{\overline{r} N v^*}{kT} \left[ \sum_{i=1}^n \psi_i P_i^* \left( \frac{1}{\tilde{v}_i} - \frac{1}{\tilde{v}} \right) \right] + \frac{\overline{r} N v^*}{kT} \sum_{j=2}^n \sum_{i=1}^{j-1} \psi_i \theta_j \left( \frac{X_{ij}}{\tilde{v}} - T \tilde{v}_i Q_{ij} \right)$$
(2.41)

where  $\psi_i$  is the segment fraction of component i,  $\theta_i$  is the surface fraction of segment *i*, and c represents the total external degrees of freedom. The spinodal and binodal equations are even more complex, therefore the reader is directed to [14, 17].

One of the key results from application of the equation of state approach to predicting phase behavior is the observation that *lcst* behavior can be predicted based upon a non-combinatorial contribution to entropy inherent with this formalism. The Flory-Huggins lattice model theory is an incompressible model that does not allow for the compressibility effects on the system thermodynamics. For equation of state approaches that allow for compressibility effects, the miscibility condition expressed by Eq. 2.2 [18] becomes:

$$\left(\frac{\partial^2 \Delta G_m}{\partial \phi_i^2}\right)_V + \left(\frac{\partial V}{\partial P}\right)_{T,\phi_i} \left(\frac{\partial^2 \Delta G_m}{\partial \phi_i \partial V}\right)^2 > 0$$
(2.42)

As  $\left(\frac{\partial V}{\partial P}\right)_{T,\phi_i} < 0$  and  $\left(\frac{\partial^2 \Delta G_m}{\partial \phi_i \partial V}\right) \ge 0$ , the compressibility nature is a negative contribution

towards achieving miscibility. However, by allowing an interaction parameter which varies with temperature, the ability to predict *lcst* behavior offered considerable interest when initially recognized by McMaster [14]. The equation of state theories also allow a prediction of the effect of thermal pressure coefficient and thermal expansion coefficient differences on the resultant phase diagram. An increase in the thermal expansion coefficient difference ( $\alpha_1 - \alpha_2$ ) results in decreasing the free energy of mixing and shifting the miscibility curve downward. An increase in the thermal pressure coefficient difference ( $\gamma_1 - \gamma_2$ ) also shifts the miscibility curve down and shifts the critical composition. The generalized behavior of the phase diagram predicted by McMaster's analysis of the Flory equation of state as function of several variables is illustrated in Fig. 2.5 (a, b, c, d). Qualitative trends for achieving miscibility predicted by this analysis include the observation that  $T^*$  values should be similar for the components. If  $T_1^* > T_2^*$ , then  $P_1^* > P_2^*$  to balance the  $T_i^*$  mismatch to maintain miscibility. The  $\alpha$  (thermal coefficient of expansion) values should be similar to maintain miscibility. Different  $\alpha$  values are the primary cause for *lcst* behavior as predicted by the Flory equation of state. In the absence of specific interactions and when  $X_{12}$  and  $Q_{12}$  are essentially zero, miscibility will be observed when  $\alpha_1 = \alpha_2$  and  $\gamma_1 = \gamma_2$  [16]. This was noted to be the case for structurally similar blends of different polyethersulfones and polyetherimide/poly(ether ether ketone) blends. This situation would also be the case for structurally similar polymers such as the miscible blend of the isomeric polymers poly(methyl acrylate) and poly(vinyl acetate). This situation corresponds to matched solubility parameters for non-interacting polymeric components.

While *lcst* behavior has been generally considered to be a consequence of the noncombinatorial entropy of mixing predicted by equation-of-state models, the experimental observation that  $\Delta H_m$  for polymer blends with specific interactions increases to more positive values with increasing temperature implies that  $\chi_{12}$  (and  $B_{12}$ ) are indeed temperature dependent with the potential for *lcst* behavior. The Flory EOS approach does not adequately predict the phase behavior of polymer blends exhibiting specific interactions. Comparison of the Flory EOS with experimental data on hydrogen bonding blends (ethylene-vinyl acetate copolymer blends with chlorinated polyethylene and PVC with poly(n-butyl acrylate)) showed poor agreement with prediction of the *lcst* position [19]. A modification of the Flory EOS approach (termed oriented quasichemical approximation) to account for nonrandom orientation present for specific interactions was evaluated and showed good agreement with prediction of lower critical solution temperatures experimentally observed [19].

Additional examples of the application of the Flory EOS to polymer blends include polystyrene/poly(vinyl methyl ether) [15, 20, 21], oligomeric polystyrene/polybutadiene [22], ethylene-vinyl acetate/chlorinated polyethylene [23], poly( $\varepsilon$ -caprolactone)/PVC [24], poly-(ether sulfone)/poly(ethylene oxide) [25].

The other equation of state model widely noted is the Sanchez-Lacombe lattice fluid theory [26–28]. The Sanchez-Lacombe equation of state is:

$$\tilde{P}\tilde{v}\tilde{T} = -\tilde{v}[\ln(1-\tilde{\rho}) + (1-1/r)\tilde{\rho}] - 1\tilde{T}\tilde{v}$$
(2.43)

where  $T^* = \varepsilon^* / k$  ( $\varepsilon^*$  is the characteristic interaction energy);  $kT^* = P^*V^*$ ;  $r = M(P^*/kT^*\rho^*)$ and  $\tilde{\rho} = 1/\tilde{\nu}\rho/\rho^*$  which reduces to:

$$\tilde{\rho}^2 + \tilde{P} + \tilde{T}[\ln(1-\tilde{p}) + (1-1/r)\tilde{\rho}] = 0$$
(2.44)

as 1/r goes to zero at high molecular weight then:

$$\tilde{p}^2 + \tilde{P} + \tilde{T}[\ln(1 - \tilde{p}) + \tilde{p}] = 0$$
(2.45)

The characteristic pressure for a binary mixture for the Sanchez-Lacombe EOS is expressed as:

$$P^* = \phi_1 P_1^* + \phi_2 P_2^* - \phi_1 \phi_2 \Delta P_{12}^* \tag{2.46}$$

where  $\Delta P_{12}^* = P_1^* + P_2^* - 2P_{12}^*$ .  $\Delta P_{12}^*$  has similarities to the binary interaction density parameter,  $B_{12}$ , and negative values of  $\Delta P_{12}$  predict miscibility.

The Sanchez-Lacombe EOS has been applied to PMMA/SAN [29], polycarbonate (PC), tetramethyl polycarbonate (TMPC) and poly( $\epsilon$ -caprolactone) binary and ternary blends [30],

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Figure 2.5: Generalized phase diagrams from equation of state predictions involving key variables (adapted from reference: McMaster, L. P., *Macromolecules*, (1973) 6, p. 760, copyright (1973) American Chemical Society)

polystyrene/polyisoprene and polystyrene/poly(cyclohexyl methacrylate [31] and styrene-maleic anhydride copolymers/polymethacrylates [32].

Additional examples of equation of state models include the lattice gas model (Kleintjens et al, [33, 34], Simha-Somcynsky hole theory [35], Patterson [36], the cell-hole theory (Jain and Simha [37-39], the perturbed hard-sphere-chain equation of state [40, 41] and the modified cell model (Dee and Walsh) [42]. A comparison of various models showed similar predictions of the phase behavior of polymer blends for the Patterson equation of state, the Dee and Walsh modified cell model and the Sanchez-Lacombe equation of state, but differences with the Simha-Somcynsky theory [43]. The measurement and tabulation of PVT data for polymers can be found in [44].

## 2.2 Phase Behavior

### 2.2.1 Miscible versus Immiscible Blends

Miscibility in the context of polymer blends is defined as the degree of mixing to yield properties (e.g., glass transition temperature, permeability) expected of a single phase material. This does not imply ideal mixing at the segmental level. Concentration fluctuations of miscible polymers would be expected to be of the order of several nanometers. In fact, many blends noted to be miscible show structure of the order of several nanometers when sensitive methods (e.g., small-angle neutron scattering (SANS)) are employed even when the thermodynamic criteria for miscibility is satisfied. In other cases, a single  $T_g$  can be present but a broad transition is observed, indicating microheterogeneous structure, possibly of the order of 10s of nanometers. The nanostructure of such blends indicates a large number of phases with varying compositions exist. This can be the case where copolymers with varying composition have been blended with homopolymers. The use of the glass transition temperature behavior to ascertain miscibility has not always been universally accepted as the glass transition is not a thermodynamic property. However, where blends have met the thermodynamic criteria (e.g., cloud point measurements), excellent agreement with glass transition measurements has allowed for the use of the  $T_g$  as an acceptable criteria for miscibility or immiscibility.

The phase diagrams for polymer mixtures can take many forms, as noted in Fig. 2.6. where single phase and phase separated regions exist in the composition-temperature range depicted. Many miscible systems (a) exhibit miscibility over the entire composition-temperature range where both polymers exhibit thermal stability. Miscible systems where the level of miscibility is borderline will often show phase separation within the experimentally determined

Miscible a	Phase separated b	lest c
d ucst	e	f
g	h	i

Figure 2.6: Phase diagrams observed with polymer-polymer blends (shaded areas represent phase separated regions). The y-axis for each diagram represents temperature and the x-axis represent volume fraction



Figure 2.7: Phase diagrams of PS/PnPMA blends with changes in molecular weight (reproduced with permission from reference: Ryu, D. Y., Park, M. S., Chae, S. H., Jang, J., Kim, J. K. and Russell, T. P., *Macromolecules* (2002) 35, p. 8676, copyright (2002) American Chemical Society)



Figure 2.8: Phase diagram of deuterated PS and PnPMA. Closed loop behavior at higher pressures (bar): triangle (97 bar); square (117 bar); inverted triangle (138 bar); diamond (166 bar); star (186 bar).T<sub>g</sub> line is the Fox equation prediction. (reproduced with permission of reference:Ryu, D. Y., Lee, D. H., Jang, J., Kim, J. K., Lavery, K. A. and Russell, T. P., *Macromolecules* (2004) 37, p. 5851, copyright (2004) American Chemical Society)

Polymer 1	Polymer 2	lcst/ucst	Reference
PS	PVME	lcst	48-50
PEO	Poly(ether sulfone) (PES)	lcst	51
PS	Tetramethyl Bis A polycarbonate	lcst	52, 53
PEA	PVF <sub>2</sub>	lcst	54
PS	Poly(o-chlorostyrene)	lcst. ucst	55
SAN	NBR	lcst, ucst	56
PMMA	Polycarbonate (PC)	lcst	57
PS	Poly(styrene-co-4 bromostyrene)	ucst	58
PC	Poly( $\varepsilon$ -caprolactone) (PCL)	lcst	59
PVF <sub>2</sub>	PMA, PEA, PMMA, PEMA	lcst	59
PMMA	SAN (28% AN)	lcst	14, 59
PMMA	SAN (32.8% AN)	lcst	60
PCL	Poly( <i>D</i> , <i>L</i> -lactide)	lcst	61
Li salt of sulfonated PS	Methylated polyamide (poly(N,N'-dimethyl sebacamide)	lcst	62
PMMA	PVC	lcst	63
PMMA	PEO	lcst	63
PC	Li salt of sulfonated PS	ucst	64
PHE	PVME	lcst	65,66
SAN	PCL	lcst	49
PS	Poly(4-methyl styrene)	ucst	67
PS	Poly(phenylmethylsiloxane) (oligomer)	ucst	68
Chlorinated PE	Chlorinated polybutadiene	ucst	69
PS	Carboxylated PPO	lcst, ucst	70
PPO	Poly( $\alpha$ -methyl styrene)	lcst	71
PMMA	$\alpha$ mS/AN (32 wt% AN)	lcst	72
PS	Poly(styrene-co-p-bromostyrene)	ucst	73

Table 2.1: Polymer Blends Exhibiting *lcst* and/or *ucst* Behavior

composition-temperature space. Lower critical solution temperature (*lcst*) (c) and upper critical solution temperature (*ucst*) (d) have been observed in polymer blends, and both were observed in rare cases (e). The hour glass diagram depicts overlapping *lcst* and *ucst* behavior (f). A study involving polystyrene-poly(n-pentyl methacrylate) reported *lcst*, *ucst* and hourglass behavior [45]. At low molecular weight for both polymers (range of 7000  $M_n$ ), both *lcst* and *ucst* behavior was observed. With a slight increase in the PS molecular weight, the hourglass phase diagram was experimentally observed, as shown in Fig. 2.7. The most common case is

the immiscible polymer blend where the phase separated region comprises the majority of the temperature-composition space (b). With all immiscible blends, each phase will contain both polymers; however, with highly immiscible blends the concentration of the other polymer in a polymer rich phase will be extremely low and have an undetectable influence on the properties of that phase. Double *lcst* (g) or double *ucst* (h) behavior can be obtained via the equation of state theory predictions and in rare cases have been experimentally observed and predicted from the equation of state models [24, 46]. All of the diagrams noted in Fig. 2.6 have been experimentally observed and can be predicted from theory. Examples of polymer blends exhibiting *lcst* and/or *ucst* behavior are listed in Table 2.1. In very rare cases, a closed loop can occur in the phase diagram (noted in low molecular weight systems also). This has been observed for a blend of deuterated polystyrene and poly(n-pentyl methacrylate) subjected to higher pressures (Fig. 2.8) [47]. At low pressure, the more typical *lcst* and *ucst* behaviors are noted.

## 2.2.2 Spinodal Decomposition and Nucleation and Growth

When a single phase mixture crosses the phase boundary into either the metastable region or the unstable region, phase separation will occur. This phase separation can occur by temperature change, by solvent removal, by non-solvent addition, by applied shear forces or by pressure change. For the discussion of the phase separation process, the temperature change will be employed as the method of phase separation. Two methods of phase separation, nucleation and growth and spinodal decomposition, can occur depending on where the phase boundary is traversed. Nucleation and growth is a more familiar phase separation mechanism and is often associated with crystallization from solution. Spinodal decomposition is less common and has been observed with metal alloys and inorganic glasses. In the metastable region of the phase diagram, only nucleation and growth can occur. Nucleation and growth yields a phase separated region that maintains a constant concentration and increasing size with time. The diffusion coefficient is considered positive, as diffusion occurs from a region of high concentration through a region of lower concentration to the phase separated surface. Spinodal decomposition occurs in the unstable region of the phase diagram and results from low amplitude concentration fluctuations spontaneously growing into phase separated regions. Spinodal decomposition yields a phase separated region that exhibits a varying composition but a constant size (at early stages of the process) as time increases. In intermediate stages in spinodal decomposition, the periodicity of structure will start increasing as percolation of the network occurs allowing liquid flow. At the later stages of separation, both processes can exhibit coalescence of particles, thus the morphology can coarsen depending upon the surface forces and viscosity. The diffusion coefficient for spinodal decomposition is considered negative as the separation of both components involves diffusion through regions of lower concentration to higher concentration. Spinodal decomposition generally yields an interwoven (co-continuous) structure. The illustration and contrast of both processes is shown in Figs. 2.9 and 2.10.

To obtain spinodal decomposition exclusively, a minor temperature change going through the critical point is required. Spinodal decomposition may occur if the metastable region is traversed rapidly into the unstable region. One question not well-answered in the literature



Figure 2.9: Comparison of phase separations processes (spinodal decomposition compared to nucleation and growth)



Figure 2.10: Generalized morphology of spinodal decomposition and nucleation and growth phase separation processes at the early stages of separation

involves the combination of these separation processes. Another question is: can spinodal decomposition (once it reaches a critical size) provide the nucleus for nucleation and growth? At the early stages of spinodal decomposition, the kinetics of phase separation can be assessed by the formalism of Cahn-Hilliard [74]. The change in the chemical potential in the early stages of spinodal decomposition is expressed by:

$$\mu_1 - \mu_2 = \frac{\partial \Delta G'}{\partial \psi_1} - 2K\nabla^2 \psi_1 \tag{2.47}$$

where  $\psi_1$  = segment fraction,  $\Delta G'$  is the free energy density, *K* is the gradient energy coefficient which can be determined from polymer dimensions, experimentally, or from the expression:

$$K = RT\chi_{12}l^2/6\nu_1$$
 (2.48)

where *l* represents a length in the range of molecular dimensions termed the Debye interaction length given by  $l = \overline{r}\sqrt{3}$ ; where  $\overline{r}$  is the root mean square of the end-to-end distance of a polymer chain and  $v_1$  equals the molar volume of polymer 1 [75]. Without going through the derivation which has been presented elsewhere [75], the most rapidly growing wavelength dominating spinodal decomposition is expressed by:

$$\lambda_m = \frac{2\pi}{\beta_m} = 2\sqrt{2\pi} \left[ \left( -\frac{1}{2K} \right) \frac{\partial^2 G}{\partial v_1^2} \right]^{-1/2}$$
(2.49)

where  $\beta_m$  = maximum wave number (cm<sup>-1</sup>). Van Aartsen [76] derived the equation relating  $\lambda_m$  to the spinodal temperature,  $T_s$ , (*lcst*), where *l* is the Debye interaction length and *T* is the measurement temperature:

$$\lambda_m = 2\pi l \left[ 3 \left( \frac{T - T_s}{T_s} \right) \right]^{-1/2} \tag{2.50}$$

At the latter stages of spinodal decomposition (and also nucleation and growth), coarsening of the structure occurs due to interfacial forces(often referred to as Ostwald ripening). The expression of the droplet size-time relationship (Lifshitz-Slyozov expression [77]) is:

$$d^{3} = d_{0}^{3} + 7.11\gamma_{12}(X_{e}\nu_{m})Dt / RT$$
(2.51)

where d = particle diameter (time = t),  $d_o = \text{particle}$  diameter after initial phase separation,  $y_{12} = \text{interfacial tension}$ ;  $X_e = \text{equilibrium}$  mole fraction of the particle rich constituent in the matrix;  $v_m = \text{molar volume}$  of the particle phase. At the latter stages of phase separation, the morphology differences between nucleation and growth and spinodal decomposition are less pronounced. Matsuoka [78] investigated the computer simulation of spinodal decomposition of polymer blends as described by the Cahn-Hilliard model. The coarsening of the structure at latter stages of the phase separation process was clearly evident.

Experimentally, the binodal temperature can be easily determined by cloud point measurements. The determination of the spinodal temperature is much more difficult. One method involves the extrapolation of the scattered light intensity from the homogeneous region. The reciprocal of the scattered light intensity,  $1/[R_{\theta}^2]_{\theta=0}$ , will go to zero as the spinodal is approached. Thus a plot of  $1/[R_{\alpha}^{2}]_{\theta=0}$  versus temperature will allow determination of the spinodal temperature. In order to improve the extrapolation, several methods have been employed, including rapid quenching of a thin film of the polymer blend samples into the metastable region between the binodal and spinodal and determining the light scattering before the nucleation and growth process can commence. A variation of this procedure termed pulse-induced critical scattering utilized a sample cell containing microliters of the polymer blend and rapidly heating and cooling the sample to various positions above and below and binodal curve (for a *lcst*) (reverse for a *ucst*) and measuring the scattering [79, 80]. This procedure works well for low molecular weight/low viscosity mixtures such as polymer-solvent or oligomeric mixture combinations, however, is less applicable for high molecular weight polymers [81]. A centrifugal homogenizer was developed to allow applicability to higher molecular weight polymer blends [82].

## 2.3 Solubility Parameter Concepts

The concept of solubility parameters to characterize interactions in liquids was introduced by Scatchard [83] and developed further by Hildebrand and Scott [3]. With liquids, the solubility parameter,  $\delta_p$ , was defined as the square root of the cohesive energy density (CED):

$$\delta_{p} = (\Delta E_{\nu} / V)^{1/2} = (CED)^{1/2}$$
(2.52)

where  $\Delta E_{\nu}$  = the energy of vaporization. Solubility parameters range from below 12 (MPa)<sup>1/2</sup> for fluorocarbon condensable gases to 30 (MPa)<sup>1/2</sup> (mercury, liquid metals). While the concept was developed for liquids, it has been applied to polymers by determination of the swelling parameters of lightly crosslinked polymers in a large number of solvents with well-known  $\delta$  values. The solubility parameter of the solvents at the position of highest swelling of the crosslinked polymer is considered the solubility parameter for the polymer. Other methods include determination of intrinsic viscosity (where solvents with similar solubility parameters allow for chain expansion, thus increased viscosity) and inverse phase gas chromatography. Typical values of polymer solubility parameters noted in the literature are listed in Table 2.2. The experimental range for some polymers is quite large due in part to the difference in methods employed.

Small [90] observed that the solubility parameters of polymers could be calculated using group contribution approaches. Additional group contribution approaches have been noted by Hoy [91], van Krevelan [86], and Coleman et al. [85]. The units employed for  $\delta_p$  are (MPa)<sup>1/2</sup>, (J/cm<sup>3</sup>)<sup>1/2</sup> or (cal/cm<sup>3</sup>)<sup>1/2</sup> (1 (MPa)<sup>1/2</sup> = 1 (J/cm<sup>3</sup>)<sup>1/2</sup> = 0.489 (cal/cm<sup>3</sup>)<sup>1/2</sup>)

The group contribution method for predicting solubility parameters employs the expression:

$$\delta_P = \rho \left| \frac{\Sigma F_i}{M} \right| = \frac{\Sigma F_i}{\nu} \tag{2.53}$$

where  $F_i$  is the molar attraction constant; M = molecular weight of the repeat unit (molar mass); v = molar volume. Values of v can be estimated also by group contribution methods ( $v = \Sigma v_r$  or  $\Sigma v_g$ ), where  $v_r$  is the molar volume group contribution in the rubbery amorphous state and  $v_g$  is the molar volume group contribution in the glassy amorphous state. Table 2.3 lists examples of group contribution values for  $F_i$ ,  $v_r$  and  $v_g$ . The approach by Coleman et al. [85] employs a specific set of v values designated by  $v^*$  and not restricted to the glass or rubber state.

As a sample calculation, polystyrene will be employed:

		Data from Small			man et al.
	# uni	ts F <sub>i</sub>	Vg	$F_i$	$\nu^*$
-CH <sub>2</sub> -	1	272	15.85	270	16.5
-CH<	1	57	9.45	47	1.9
$-C_6H_5$	1	1504	72.7	1504	75.5
		1833	98.0	1821	93.9
		<u>calculated</u>	experimen	ntal <u>calcu</u>	ilated
$\delta_{\rm p}~({ m MPa})^{1/2}$		18.7	15.6-21	.1 19	9.4
Ŵg		98	99		

Polymer	Polymer	Coleman	Small	Van	Other
	Handbook	calcu-	calc.	Krevelan	Values (Ref)
	range (average)	lated [85]	[86]	calc. [86]	
	[84]				
Polytetrafluoroethylene	12.7 (12.7)		12.3	13.1	
Polydimethylsiloxane	14.9–15.6 (15.3)		12.5	-	
Polybutadiene	14.7–17.6 (16.7)	16.6	16.5	16.5	
Polyisoprene (1,4)	15.2-20.5 (16.7)	16.6	16.5	17.0	
Polyisobutylene	14.5–17.0 (16.2)	14.7	14.5	16.8	
Polyethylene	15.8–18.0 (16.5)		16.9	17.2	
Polypropylene	18.8–19.2 (19.0)		15.4	17.0	
Polymethylmethacrylate	18.6–26.3 (19.8)	18.4	18.2	18.7	
Polyethylmethacrylate	18.2–18.6 (18.4)	18.2	18.0	18.4	
Polybutylmethacrylate	14.7-18.0 (17.2)	17.8	17.9	18.2	
Poly(methyl acrylate)	20.1–21.3 (20.7)	19.6	19.6	19.0	
Poly(ethyl acrylate)	18.8–20.4 (19.4)	19.0	19.2	18.6	
Poly(propyl acrylate)	18.4–18.5 (18.4)	18.6	18.8	18.5	
Poly(n-butyl acrylate)	17.4–19.8 (18.4)	18.2	18.6	18.3	
Poly(2-ethyl hexyl acrylate)		17.3	17.6		
Poly(vinyl acetate)	18.0–22.6 (19.7)	19.6	19.7	19.0	
Polystyrene	15.6–21.1 (18.5)	19.4	18.7	19.2	
Poly(vinyl chloride)	19.2–22.1 (19.9)	20.3	19.5	19.7	
Bis A polycarbonate					
Poly(propylene oxide)		17.4	16.0	19.1	
Poly(ethylene oxide)	20.2 (20.2)	19.2			
Polymethacrylonitrile	21.0-21.9 (21.5)	24.3	20.5	25.4	
Polyacrylonitrile	25.3–31.5 (27.1)	28.2	26.0	27.8	
Poly(ethylene terephthalate)	21.9 (21.9)	23.5	21.9	21.3	
Poly(phenylene oxide) (PPO)		19.1	19.2		
Poly(vinylidene chloride)	25.0 (25.0)		20.9	21.6	20.9 [87]
Chloroprene rubber					16.7–18.9 [88]
Cellulose (di) nitrate					21.6 [88]
Cellulose (di) acetate					21.7 [88]
Nylon 6,6 (PA66)					27.8 [88]
Nitrile rubber (25% AN)					19.2–19.4 [88]
Nylon 66 (PA66)					27.8 [89]
Poly(phenylmethyl siloxane)					18.4 [89}
Natural rubber (NR)					16.6 [89]
Ethyl Cellulose					21.1 [89]
Polychlorotrifluoroethylene				16.6	14.7 [89]

**Table 2.2:** Solubility Parameters  $(\delta_p (MPa)^{1/2} \text{ for Selected Polymers})$ 

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Group	Small	Hoy	Van	Coleman	Vg	$\boldsymbol{v}_r$	$v^*$
-			Krevelan	et al.	5		
-CH <sub>3</sub>	438	303	419	446	23.9	22.8	31.8
-CH <sub>2</sub> -	272	268	280	270	15.85	16.45	16.5
-CH<	57	176	139	47	9.45	9.85	1.9
>C<	-190	65	0	-198	4.6	4.75	-14.8
-CH=	227	250	223	231	_	13.9	13.7
>C=	39	172	82	37	_	-	-2.4
Phenyl	1504	1397	1516	1504	72.7	64.65	75.5
Phenylene	1346	1442	1377	1333	65.5	61.4	58.8
-0-	143	235	256	194	10.0	8.5	5.1
-CO-	563	538	685	536	13.4	_	10.7
-COO- (general)	634	669	512	610	23.0	24.6	19.6
-COO- acrylic	634	669	512	610	18.25	21.0	19.6
-Cl	532	419	471	540	19.9	18.4	23.9
-CN	839	726	982	872	19.5	-	23.6
-CF <sub>2</sub> -	307	235	_	_			_
-CF <sub>3</sub>	560						
-NH <sub>2</sub>	_	406	204	563			18.6
>NH		368	286	292			8.5
-S-	460	428			17.8	15.0	

**Table 2.3:** Group contribution values for calculating solubility parameters  $F_i$  ( $J^{1/2}$ cm<sup>3/2</sup>mol<sup>-1</sup>) Molar Volume (cm)<sup>3</sup>mol<sup>-1</sup>

PPO/PS blends are miscible with at best only a modest specific interaction and  $B_{12}$  and  $\chi_{12}$  values determined by various methods yielding only small negative values. This indicates that similar solubility parameters should exist. The solubility parameter of PPO calculated from Small and Coleman et al. are shown below:

	Data from Small			Colen	Coleman et al.	
	# units	$F_i$	$v_g$	$F_i$	$v^*$	
Phenylene	1	1346	65.5	1333	58.8	
-CH <sub>3</sub>	2	876	47.8	892	63.6	
-0-	1	143	10.0	194	5.1	
		2365	123.3	2419	127.5	
$\delta_p (MPa)^{1/2} =$		19.2 (Small)		19.0 (Col	19.0 (Coleman et al.)	

The values for PPO calculated by both methods show minor differences in the solubility parameters for PPO and PS with averaged results showing  $\delta_p(\text{PPO}) = 19.1(\text{MPa})^{1/2}$  and  $\delta_p(\text{PS}) = 19.05 \ (\text{MPa})^{1/2}$ . This agrees well with the expectation of matched solubility parameters with minor contributions of specific interactions and combinatorial entropy to yield miscibility. Note that these calculations are based on amorphous polymers or above the crystalline melting points of crystalline polymers.

The use of the solubility parameter concept has been extended to predict values of  $\chi'_{12}$ , and  $B_{12}$  from the expression involving the heat of mixing (see Section 2.1.2)

$$\frac{\Delta H_m}{V} = \phi_1 \phi_2 (\delta_1 - \delta_2)^2 \tag{2.54}$$

$$B_{12} = (\delta_1 - \delta_2)^2 \qquad \chi_{12}' = (\delta_1 - \delta_2)^2 / RT$$
(2.55)

The solubility parameter as initially proposed is for non-polar and non-associating molecules. Thus, for polymer blends, the best agreement is achieved for purely dispersive interacting blends (e.g., polyolefins).

Note that values of  $(\delta_1 - \delta_2)^2$  will always be zero or positive, leading to positive values for  $\Delta H_m$ thus immiscibility in the limit of very high molecular weight. With lower molecular weight and basically values of  $(\delta_1 - \delta_2)^2$  equal or very close to zero, miscibility can be achieved from the small contribution of combinatorial entropy. At equal molecular weights of the components (density = 1.0 g/cc), it can be shown from Eq. 2.27 that  $(\delta_1 - \delta_2)_{cr} = (2RT/M)^{1/2}$ . While the solubility parameter approach has relevance to polymer blends with very weak interactions, it must be considered with other approaches in cases of strong specific interactions between polymers. In the formalism developed by Coleman et al. [92], a practical guide for predicting the miscibility of polymers employed the solubility parameter difference to determine the strength of specific interactions needed to obtain miscibility. The critical solubility parameter difference  $(\Delta \delta_p)_{cr}$  relative to the strength of specific interactions needed to achieve miscibility was classified as:

Interaction	$(\Delta \delta_{p_{cr}}(\mathrm{MPa})^{1/2})$
Dispersive Forces	< 0.2
Polar Forces	< 1.0
Weak specific interactions	< 2.0
Moderate specific interactions	< 4.0
Strong specific interactions	< 6.0

This observation by Coleman et al. [92] has also been discussed by Walsh and Cheng [93], where the heat of mixing is proposed to be the sum of dispersive and specific interaction contributions:

$$\Delta H_m = \Delta H_m \text{ (dispersive)} + \Delta H_m \text{ (specific)}$$
(2.56)

This approach was applied to experimental data of analog compounds of PVC and poly(meth)acrylates as shown in Fig. 2.11. The specific interaction  $\Delta H_m$  was assumed proportional to the C=O concentration. The experimental heat of mixing was determined via analog calorimetry. The predicted  $\Delta H_m$  illustrates a window of miscibility between C=O values of 0.1 and 0.32 weight fraction (for the poly(meth)acrylates) in the range of observed experimental results on analog compounds and also low molecular weight polymer blends.

Shaw [52] noted that an improved procedure for utilizing the solubility parameter method to predict polymer phase behavior involved matching the polar and dispersive contributions to the solubility parameter ( $\delta_{pol}$  and  $\delta_d$ ) to achieve a better potential for miscibility. Other approaches utilizing multidimensional solubility parameter matching includes Hansen [94,



**Figure 2.11:** Specific interaction and dispersive contributions for PVC/poly(meth)acrylate blends compared with experimental heat of mixing results (see Eq. 2.56) (W<sub>C=0</sub> is the weight fraction of carbonyl units in the poly(meth)acrylates) (reproduced (replotted) from reference: Walsh, D.J. and Cheng, G.L., *Polym*. (1984) 25, p. 499, with permission from Elsevier)

95], where the solubility parameter was expanded to include three contributions (dispersive, polar, hydrogen bonding). This approach has been useful for predicting solvents for various polymers by matching the various contributions with solvents having similar values (within a spherical volume in a 3-dimensional plot). Some attempts to employ this approach for polymers have been made [96, 97], but they are not of sufficient predictive ease/utility to be universally employed. Specific examples of the Hansen solubility parameters for selected polymers are given in Table 2.4.

Polymer	$\delta_p$	$\delta_d$	$\delta_{pol}$	$\delta_h$
Polystyrene	22.47	21.28	5.75	4.30
Poly(vinyl chloride)	21.42	18.23	7.53	8.35
Poly(methyl methacrylate)	22.69	18.64	10.52	7.51
Poly(vinyl acetate)	25.66	20.93	11.27	9.66
Polyisobutylene	15.47	14.53	2.52	4.66
Poly(ethyl methacrylate)	20.46	17.60	9.66	3.97
Polyacrylonitrile	25.27	18.21	16.16	6.75
Nylon 6,6	22.87	18.62	5.11	12.28
Cellulose acetate	25.08	18.60	12.73	11.01
Poly(ethylene terephthalate)	21.54	19.44	3.48	8.59

**Table 2.4:** Hansen Solubility Parameters ( $\delta_i$  (MPa)<sup>1/2</sup>) for Selected Polymers (values selected from [84])

The solubility parameter can be used as a guide (as noted [92]) but lacks the ability to predict the specific interactions so important in achieving miscibility in many polymer blends. Reviews of the solubility parameter concept applied to polymers and polymer blends include [97, 98].

## 2.4 Specific Interactions

In order to achieve the negative heat of mixing required by high molecular weight polymers, specific interactions play a key role in many observed miscible systems. Purely dispersive interactions (such as those exhibited by polyolefins) would not be considered strong enough to provide miscibility. Intramolecular repulsion is another method to achieve miscibility and will be discussed in the next section. As with mixtures of low molecular weight liquids, several types of specific interactions are possible including hydrogen bonding, acid-base (Lowry-Brönsted or Lewis), charge transfer, dipole-dipole, ion-dipole, induced dipole-dipole,  $\pi$ -hydrogen bonding, n- $\pi$  complex formation, and  $\pi$ - $\pi$  complex formation. Examples of polymer miscibility attributed to these interactions are given in Table 2.5. The relative strength of these interactions range from 0.4–0.5 kJ/mol for dispersive interactions to 2–25 kJ/mol for the range of hydrogen bonding strength. Covalent bonds are typically in the range of 100 kJ/mol.

#### 2.4.1 Hydrogen Bonding Interactions

The most prevalent specific interaction studied in polymer blends is hydrogen bonding. A treatise on specific interactions [92] in polymer blends primarily discussing hydrogen bonding has covered this subject in detail. Hydrogen bonding characteristically involves a bond between hydrogen (proton donor) and another group (proton acceptor or electron donor). Many hydrogen bonding groups have the capability of being donors and acceptors for both electrons and protons. They thus have the capability of self-hydrogen bonding (self-association). Specific examples of hydrogen bonding between donor-acceptor groups involving self association are illustrated below:



The hydrogen bonding capability of specific structural groups has been noted by Burrell [99] and Lieberman [100]. The donor, acceptor and donor/acceptor groups are listed in Table 2.6 with the relative hydrogen bonding strength noted. The hydrogen bonding strength is based