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Course Notes of Chapter 5

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1. Introduction: Polymer Blends

A polymer blend is the combination of two or more existing polymers in order to create a new material with different physical properties (mechanical, barrier, etc.), without the need to develop new synthesis techniques, which can be extremely expensive. The key to this method is to be able to adjust the properties of the new material to make it suitable for use, through both the correct selection of the polymers it is made of and the mixing technique. This controls the miscibility of the components of the mixture as well as the morphology of an immiscible mixture. It is therefore essential to understand under which conditions a mixture of two or more chemically distinct polymers will show phase separation. In the case of immiscible thermoplastics, it is then necessary to control the morphology by adjusting the processing parameters according to the rheological properties of the components as well as the quality of the interface between the different phases, which can be "compatibilized" by using reactant systems or block copolymers, for example.

1.1 Can a Polymer Dissolve in Another?

The question arises because we will see that the theory according to Flory and Huggins implies that two chemically distinct polymers are immiscible, if their molar masses are high. Indeed, it is observed that most thermoplastics are immiscible. However, there are exceptions, including some commercial systems (Slides 364 and 365).

1.2 Morphology of Immiscible Systems

Immiscibility involves phase separation, at least in certain ranges of concentrations and temperature, if the pressure is kept constant. In general, this behavior is represented by a phase diagram, which can be modeled by considering the evolution of the Gibbs free energy of mixing, ΔG_{m}, assuming that the system is at equilibrium. However, the morphologies that result from phase separation are, in general, strongly influenced not only by thermodynamics, but also by the thermomechanical history of the mixture and the interface between the phases.

1.3 Morphology of Copolymers

Copolymers represent an extreme case of a mixture, where the components of the mixture (the monomers) are linked by covalent bonds. In the case of a block copolymer whose blocks are immiscible, phase separation may take place, but the size and shape of the domains of each phase will depend on the size of the blocks. This is called microphase separation. On the other hand, in the case of a random copolymer, the morphology will be homogeneous, whatever the nature of the monomers.

2. Simple Polymer Solutions

2.1 Thermodynamics of Mixtures

A mixture is equivalent to the simple solution that we have already covered during our discussion of the solubility parameter (Chapter 3.1), where we assumed that a solution, that is a homogeneous mixture (or miscibility), must be favored, if the change in cohesion energy ΔE is low. However, for the solution to be thermodynamically stable, the difference in free energy before and after the formation of the mixture must be negative (note that this is a necessary condition, but not sufficient, as we will see later). Since most of the time we are interested in mixtures at atmospheric pressure, this condition can be expressed using the Gibbs free energy of the mixture:

$$\Delta G_m = \Delta H_m - T\Delta S_m \quad (1),$$

where T is temperature, ΔH_m is the (molar) enthalpy change during mixing, and ΔS_m is the (molar) entropy change. We will consider these two terms separately according to the approach of Flory and Huggins to a mixture of small molecules.

2.2 Mixing Entropy

According to Flory and Huggins, ΔS_m is dominated by the configurational entropy of the system, which is associated with the positions of its elements in space (not to be confused with the configuration of a molecule, which refers to the arrangement of its chemical bonds). We will start by looking at the entropy configuration of mixing of a system of N_1 "small" blue molecules and N_2 gray molecules in the form of beads of identical size distributed on a network of $n = N_1 + N_2$ sites, as shown on Slide 351 in two dimensions. The number of distinguishable arrangements is given by

$$\Omega = \frac{(N_1 + N_2)!}{N_1!\,N_2!} \quad (2),$$

We place the balls on the lattice randomly. The first ball, randomly drawn, whether blue or gray, can be placed on any of the n, initially free sites. So there remains $n-1$ site free for the second ball and so on. The total number of possible arrangements would therefore be $n \times (n-1) \times (n-2)$ ... $3 \times 2 \times 1 = (N_1 + N_2)!$ if all the balls were different. However, we cannot distinguish between two balls of the same color. We must therefore divide by $N_1!$ and $N_2!$, the total number of possible arrangements of N_1 balls on N_1 sites and of N_2 balls on N_2 sites, respectively, to obtain Equation 2. The total entropy is then obtained by applying the Boltzmann formula where k is the Boltzmann constant:

$$\Delta S_m^n = -k \ln \Omega = k(\ln(N_1 + N_2)! - \ln N_1! - \ln N_2!) \quad (3),$$

Using the Stirling approximation, $\ln X! \approx X \ln X - X$, if $X \gg 1$, we get

$$\Delta S_m^n = -k\left(N_1 \ln\left(\frac{N_1}{N_1 + N_2}\right) + N_2 \ln\left(\frac{N_2}{N_1 + N_2}\right)\right) \quad (4),$$

and per mole of sites:

$$\Delta S_m = \frac{N_A}{n}\Delta S_m^n = -R(\phi_1 \ln(\phi_1) + \phi_2 \ln(\phi_2)) \quad (5).$$

$$\phi_i = \frac{N_i}{N_1 + N_2} \quad (6)$$

is the volume fraction of each component. On Slide 351, we calculated the mixing entropy per lattice side based on the microstates of a single ball but arrived at an equivalent expression.

2.3 Mixing Enthalpy for Polymer Blends

To estimate the enthalpy of mixing, we take a similar approach as used in our discussion of the solubility parameter for polymer solutions. This leads us to Flory's interaction parameter for polymer blends.

Entropic changes during mixing of polymers are negligible, and so their miscibility is usually governed by enthalpic changes (as long as specific interactions between them are absent). If the network coordination number is z, we can write

$$E_{coh}^{ii} = \frac{z}{2} N_A w_{ii} \qquad (7),$$

and we admit that

$$\Delta \mathrm{w}_{12} = \frac{w_{11} + w_{22} - 2w_{12}}{2} \approx \frac{w_{11} + w_{22} - 2\sqrt{w_{11}w_{22}}}{2} = \frac{(|\sqrt{w_{11}}| - |\sqrt{w_{22}}|)^2}{2} = \frac{\left(\left|\sqrt{E_{coh}^{11}}\right| - \left|\sqrt{E_{coh}^{22}}\right|\right)^2}{zN_A} \qquad (8).$$

In a mixture, the probability of a contact between blue and grey balls (or species 1 and 2) is equal to $\phi_1\phi_2$ and the molar mixing enthalpy thus becomes

$$\Delta H_m = zN_A \Delta w_{12} \phi_1 \phi_2 = \left(\left|\sqrt{E_{coh}^{11}}\right| - \left|\sqrt{E_{coh}^{22}}\right|\right)^2 \phi_1\phi_2 = V_0(\delta_1 - \delta_2)^2 \phi_1 \phi_2 \equiv RT\chi\phi_1\phi_2 \qquad (9),$$

where V_0 is the molar volume of a lattice site and δ_i are the solubility parameters of the balls. Equation 9 also defines the Flory-Huggins interaction parameter,

$$\chi = \frac{\left(\left|\sqrt{E_{coh}^{11}}\right| - \left|\sqrt{E_{coh}^{22}}\right|\right)^2}{RT} = \frac{V_0(\delta_1 - \delta_2)^2}{RT} \qquad (10).$$

Note that according to this model, which admits that the interactions between the balls are purely enthalpic, χ is always positive and varies with $1/T$.

2.4 Total Energy of Mixture: Extension to Binary Mixtures Containing Polymers

For our mixture of balls, we obtain by combining Equations 1, 5 and 10:

$$\Delta G_m = RT(\phi_1 \ln(\phi_1) + \phi_2 \ln(\phi_2) + \chi\phi_1\phi_2) \qquad (11).$$

This equation, **the Flory-Huggins equation**, provides a first indication of the free energy of a binary mixture of molecules of comparable molar volume for a composition and a given T (it is in principle also valid for a condensed binary mixture of any type of objects, whether marbles, bananas or entire planets!). What about a molecular mixture, where one of the components is a polymer and the other is a solvent of low molecular weight and therefore of much lower molar volume than the polymer? We fit the model by assuming that the molecules of the polymer consist of n volume segments V identical to that of the solvent, thus defining the volume of a site in the lattice, connected by covalent bonds (Slide 355). We can also treat a mixture of two monodisperse polymers 1 and 2 by considering that their molecules are composed of chains of n_1 and n_2 (denoted as N_A and N_B on the Slide) elements of volume V_0, respectively.

Looking at Slide 355, we immediately see that the number of possible arrangements of molecules decreases sharply with n_1 and n_2, to the point where it becomes quite difficult to draw a mixture of two polymers, even for moderate values of N (10 here). We conclude that the entropy contribution to Equation 1 also decreases. We will not present the calculations here (you will find them in the standard texts), but the results are as follows:

Polymer + solvent of low molar mass:

$$\Delta G_m = RT\left(\frac{\phi_1}{n_1}\ln(\phi_1) + \phi_2\ln(\phi_2) + \chi\phi_1\phi_2\right) \qquad (12).$$

Two polymers:

$$\Delta G_m = RT\left(\frac{\phi_1}{n_1}\ln(\phi_1) + \frac{\phi_2}{n_2}\ln(\phi_2) + \chi\phi_1\phi_2\right) \qquad (13).$$

This result is independent of the choice of V_0, and it effectively implies that the entropic contribution becomes negligible for high n_1 and n_2. Since χ is always positive according to Equation 10, ΔG_m should always be positive for binary mixtures of high molecular weight polymers. **This implies that a homogeneous mixture between two polymers should always be thermodynamically unstable with respect to a macroscopically phase separated state.** In other words, all polymers should be immiscible. However, the Flory-Huggins model relies on many simplifications, such as the assumption of ideal chains (we do not consider the effect of the solvent on their conformations) with a constant volume and concentration of segments. More importantly, the actual values of χ associated with real systems can deviate significantly from the predictions of Equation 10, especially in the presence of specific interactions, which are often associated with significant changes in entropy.

2.5 Examples of Miscible Polymers

In accordance with the predictions of the Flory-Huggins equation, most polymers are indeed immiscible. Nevertheless, certain pairs of polymers are miscible, with effective negative values of χ, at least in certain temperature ranges, often associated with specific interactions, such as:

- π-π interactions of benzene units. Example: PS/PPE (PPE: poly(phenylene ether) or PPO™)
- Hydrogen bonds. Example: PVC/PCL (PCL: poly(ε-caprolactone))
- Acid-base interactions
- Ionic interactions

Miscibility is particularly favored if the specific interactions are only present in the mixture, as it is the case of hydrogen bonds in case of PVC/PCL mixtures. Such systems are often very useful from a practical point of view, allowing the physical properties of certain glassy polymers to be modified without compromising their transparency. We will see soon, for example, that a homogeneous mixture will show a T_g between values that the two individual components would show (see Chapter 3.2).

Miscible mixtures of PVC with polyacrylate, polymethacrylate, or even perchlorinated PE (random number and positions of Cl) allow the ductility and heat resistance of PVC to be improved without the need for plasticizers. Mixing PS with PPO improves its ductility and increases T_g (Noryl™ alloys, widely used in industry are an example - pure PPO is certainly ductile, but more expensive and difficult to process).

3. Immiscible Mixtures

Unlike a homogeneous system, a mixture or a block copolymer separated into two different phases will show two T_g as well as very inhomogeneous thermomechanical properties at the local level, which is essential for impact reinforcement or "rubber toughening" (see Chapter 4.3), and for the design of thermoplastic materials. However, the morphology, that is, the way in which variations in properties are distributed in space, is also very important for the synergy between the properties of the different phases: gluing a block of an elastomer to a block of a glassy polymer will not have the same effect as dispersing the elastomer in the glassy polymer on a micrometer length scale.

In general, we describe phase separation by using a phase diagram, which allows us to estimate the proportions and compositions of different phases present in a mixture at equilibrium. A phase diagram can also tell us about the mechanisms of phase separation (spinodal decomposition or nucleation and growth) when crossing a phase boundary. However, upon mixing two polymers in practice, they often remain immiscible from the starting point to the end, and the morphology depends rather on the mechanical processes used for this purpose.

3.1 Simple Phase Diagrams

We are explaining only briefly the concept of a phase diagram and the phase separation mechanisms, as you have surely encountered them in other courses. The essentials are summarized on Slides 357 and 359, namely the criteria for immiscibility and the areas of the phase diagram where phase separation is expected by spinodal decomposition or by nucleation and growth.

A binary mixture will be miscible for any composition, ϕ, if $\Delta G_{\mathrm{m}} < 0$ provided that a phase separation does not lead to a further drop in free energy. This last situation can occur if $\Delta G_{\mathrm{m}}(\phi)$ shows two inflection points, that is to say two compositions where

$$\frac{\mathrm{d}^2\Delta G_m(\phi)}{d\phi^2} = 0 \qquad (14),$$

as predicted by the Flory-Huggins Equation for certain combinations of χ, n_1 and n_2. This implies that there are two minima of $\Delta G_{\mathrm{m}}(\phi)$ and that a mixture of composition ϕ reaches its minimum energy when it separates into two phases of composition approximately ϕ_- and ϕ_+ where $\phi_- < \phi < \phi_+$ and

$$\left(\frac{\partial \Delta G_m}{\partial \phi}\right)_{\phi_-} - \left(\frac{\partial \Delta G_m}{\partial \phi}\right)_{\phi_+} = 0 \qquad (15),$$

We can then determine the volume fractions of these two phases, f_- and f_+ from

$$f_-\phi_- + f_+\phi_+ = f_-\phi_- + (1 - f_-)\phi_+ = \phi \qquad (16).$$

However, if the starting point is a homogeneous mixture and lies between the two compositions corresponding to the inflection points, small fluctuations in composition $\delta\phi$ lead to an increase in ΔG_{m}. There is therefore an activation barrier to phase separation: phase separation then proceeds by nucleation and growth. On the other hand, ΔG_{m} decreases for small fluctuations if ϕ is located between the two inflection points, where

$$\frac{\mathrm{d}^2\Delta G_m(\phi)}{d\phi^2} < 0 \qquad (17).$$

In this case, the phase separation takes place spontaneously and we speak of a spinodal decomposition.

When χ varies with temperature, which is generally the case, we can represent this information in a phase digram in space (ϕ, T), namely the locations of the minima (the “binodal” or “coexistence curve”) and the inflection points of ΔG_{m} (the “spinodal”) (Slides 357 & 359). It should be noted that this type of relatively simple phase diagram describes binary mixtures in the absence of any other phase transition, such as crystallization (compare for example with an Fe-C phase diagram!). The Flory-Huggins model predicts that $\chi \propto 1/T$, and therefore better miscibility at high T, but this may be different depending on absence/presence as well as the nature of specific interactions. For example, hydrogen bonds are more stable at low temperatures, implying an increase in χ with T. This is why we often prefer to construct a phase diagram in space (ϕ, χ/kT), especially if the diagram is derived from theoretical calculations.

Slide 359 thus shows a phase diagram for the liquid-state demixing of a binary system according to the predictions of the Flory-Huggins Equation for different values of T and the corresponding phase diagram, showing the spinodal and binodal (left Figure). On the right is shown a diagram with different types of binodal curves that binary mixtures can show: (i) a rather miscible system at low temperature characterized by a “lower critical solution temperature” for a given composition (lower critical solution temperature, LCST); (ii) rather miscible system at high temperature, characterized by an “upper critical solution temperature” (UCST); (iii) for both note the "miscibility gap".

3.2 Morphology of Immiscible Mixtures

As we saw in the previous section, when an initially homogeneous mixture separates in phase, which can result from a change in temperature or in the degree of polymerization in the case of a proceeding reaction. Indeed, phase diagrams in space (ϕ, n) where n is the degree of polymerization are very useful if one wants to understand the phase separation mechanisms in thermoset-rubber systems where the rubber becomes immiscible with the thermoset at a certain critical degree of polymerization. The resulting dispersion of rubbery domains is widely used to improve the impact resistance of epoxy resins, for example.

In general, starting from a homogeneous mixture, we cross the binodal before crossing the spinodal. Once the binodal has been crossed, sufficiently large fluctuations in composition form stable seeds capable to subsequently increase. The activation barrier to nucleation includes an interfacial term which is absent in the Flory-Huggins equation (at equilibrium a macroscopic phase separation is assumed, and therefore a negligible interfacial contribution to free energy). Indeed, the domains that result from nucleation and growth in a liquid medium initially form spheres in order to minimize their surface-to-volume ratio and therefore their interfacial energy. Minimizing interfacial energy also promotes coalescence of the domains, and a system with sufficient mobility (oil and vinegar, for example) will evolve into macroscopic phase separation. However, the very low mobility of polymers implies morphologies very far from equilibrium and therefore relatively fine dispersions of spherical domains of one phase in the other, kinetically trapped by a drop in temperature (or by crosslinking and/or an increase in T_g in thermosets).

This is because nucleation and growth are sufficiently delayed for the spinodal to be crossed before significant phase separation can take place. Beyond the spinodal, the phase separation is in principle spontaneous as long as there is no activation barrier. However, the resulting morphologies are strongly influenced by interfacial energy. They initially appear in the form of a co-continuous arrangement of local fluctuations in concentration over a characteristic distance λ_c (Slide 360) where λ_c corresponds to the concentration gradient which reinforces most rapidly: a high concentration gradient facilitates the diffusion and therefore the development of the fluctuations, but if the gradient concentration is too high, the interfacial energy becomes too great for the phase separation to be thermodynamically favorable.

However, as the spinodal decomposition advances and local concentrations approach their equilibrium values, the morphology of a liquid system tends to evolve into relatively large spherical domains of one of the phases in the continuous matrix (the other phase), according to their final proportions, or even a macroscopic phase separation, in order to minimize its interfacial energy.

In industry, blends of immiscible thermoplastics are typically mixed in the form of solid granules and then introduced into an extruder where they undergo significant shear in the molten state (Slide 361). It is then very important to control the viscosities of the matrix and the minority phase, η_1 and η_2, respectively, by adjusting the extrusion temperature as well as their molar masses, if one wants to obtain a good dispersion. To illustrate this, consider a beaker of water containing a few drops of honey (a relatively viscous substance) and a beaker of honey containing a few drops of water. It is obvious that it is easier to deform the water and therefore to disperse it by stirring the honey than vice versa. Other important parameters are the interfacial tension, γ_{12}, the initial size of the minor phase domains (the size of the granules) d, and the strain, σ, developed in these domains. We can then define a viscosity ratio:

$$\Lambda = \frac{\eta_1}{\eta_2}$$

and a capillary index

$$\mathrm{k} = \frac{d\sigma}{\gamma_{12}}$$

In general, if $\Lambda < 3.8$ and $k > 0.1$, the domains of the minor phase will be deformed, and if $\Lambda < 3.8$ and $k > 4$, we obtain a fibrillar structure. When the shear is stopped, the domains tend to return to their original shape to minimize their elastic and interfacial energy. However, if the elastic stresses relax quickly, which is usually the case in a viscous state, the fibrils transform into spherical domains whose diameter is comparable to the initial diameter of the fibrils.

There are many other methods of producing phase-separated mixtures (Slide 362). Note that in most of these examples this involves the addition of a rubbery phase to a glassy or semi-crystalline polymer with the aim of improving the resistance to rupture (rubber toughening).

3.3 Stabilization of Morphology

One of the major problems with immiscible thermoplastic blends is the lack of stability of the obtained morphology. Thus, even if the extrusion often makes it possible to obtain an optimized morphology with regard to impact resistance, for example, subsequent operations, such as injection, can significantly change this morphology. This is why emulsifiers (amphiphilic molecules) are systematically used in order to stabilize the interface between the dispersed phase and the matrix and therefore to prevent the growth of the domains of the dispersed phase in the molten state. A common example of emulsion stabilization by emulsifiers is milk, which consists of a dispersion of lipids in an aqueous medium, stabilized by phospholipids and charged proteins (k-caseins). Mechanical treatments such as butter churning or enzymatic modification by UV irradiation of these emulsifiers can nevertheless lead to coagulation, or even a macroscopic phase separation of lipids and “whey” (*Molke* or *petit-lait*).

In the case of blends of thermoplastics, the emulsifiers can be diblock copolymers of which one block is soluble in the dispersed domains and the other in the matrix. When present at interfaces, these copolymers can also improve the mechanical strength of the interface. However, this approach is not very efficient because the segregation of the copolymers at the interfaces is associated with relatively long diffusion times. Therefore, it is often preferable to form the copolymers *in situ* at the interfaces using reactive mixtures, such as polyamide 6 (PA6) blends and isotactic polypropylene functionalized with maleic anhydride (Slide 363). The NH_2 groups at the ends of the PA6 chains can react with the reactive maleic anhydride (MAH) groups grafted to iPP-g-MAH, creating graft copolymers of PA6 and iPP-g-MAH at the interfaces.

Another possibility is to synthesize elastomer particles by emulsion polymerization, and to graft chemically identical chains to the matrix at their surface in order to ensure good dispersion. This approach is widely used to improve the impact resistance of glassy polymers such as PS and PMMA, and emulsion polymerization allows particles to be produced with a variety of architectures (Slide 363).

4. Copolymers

There are two main classes of copolymers:

- random or "statistical" copolymers
- block copolymers (diblock or multiblock, linear or grafted).

4.1 Random copolymers

Statistical copolymers generally show a T_g close to the average of those of its components, weighted according to the composition. The T_g is usually low. Random copolymerization makes it possible to form homogeneous mixtures of monomers whose respective homopolymers are immiscible. Standard copolymers of commercial importance include: poly(ethylene-*co*-propylene), also known as ethylene propylene rubber or EPR. While PE and iPP are semi-crystalline polymers, EPR is a rubber because the random chain sequence of its comonomers prevents its crystallization. It can be crosslinked if a small proportion of a diene-type comonomer is added to form ethylene propylene dienemonomer (EPDM), an elastomer popular for its thermal resistance. EPR is often used for rubber toughening of iPP and PE. In the case of a reactive blend (Slide 362), the EPR is produced *in situ* at the same time as the matrix: we start by producing pure LDPE, then we increase the concentration of propylene in the reactor as the reaction progresses. This results in EPR particles with a core rich in LDPE in an iPP matrix, a material used in bumpers (*Stoßfänger* or *le pare-chocs*), for example. Poly(styrene-

co-acrylonitrile) (PSAN) is a glassy amorphous polymer that is easier to process than polyacrylonitrile (PAN) but more mechanically and thermally resistant than PS. Grafting PSAN onto polybutadiene (PBD) chains, an elastomer, under controlled conditions (e.g. emulsion polymerization) produces acrylonitrile-butadiene-styrene (ABS), a toughened rubber version of PSAN, which is widely used for any kind of inexpensive case requiring a minimum of impact resistance (household appliances, electronic devices, toy bricks etc.).

4.2 Self-Organization of Block Polymers

Phase-separated block copolymers make it possible to obtain a marked contrast of physical properties (for example based on those of an elastomer and those of a glassy polymer) on a very small scale, depending on the size of the blocks, with very resistant interfaces because they are reinforced by covalent bonds. Thus, typically at least two glass transitions and often at least one melting point are observed in this type of polymers. If the length of the blocks is well defined (monodisperse blocks), the minimum of ΔG generally corresponds to a periodic structure with a constant curvature of the interfaces (at least for diblock copolymers). The resulting morphology depends on the ratio of the block lengths (Slide 369).

4.3 Practical Applications of Block Copolymers

Among the applications of block copolymers, we can list

- Shock-resistant polymers (ABS for example)

- Thermoplastic elastomers, for example - PS-co-PBD, or "styrene-butadiene-styrene" (SBS) characterized by a “physical” crosslinking of the rubbery PBD domains by glassy domains of PS. Polyurethanes (-NHCO-R-NHCO-)$_n$, comprise rubbery domains linked by crystalline or pseudo-crystalline domains that are particularly stable because of hydrogen bonding interactions in the hard domains.

- Nanotechnology - exploitation of self-organized structures as precursors in the manufacture of periodic arrangements of inorganic nanoparticles (quantum dots), for example.

- Various functional polymers modified by addition of reagents or by grafting:

  PS-b-PBD + hydrogenation of the PBD double bonds for production of PS-b-PE (compatibilization of PS/PE mixtures)

  iPP + acrylic acid (adhesion promoter of iPP with wood, $CaCO_3$, etc.

  Cellulose (paper, cotton...) + mercury monomers, radioactive materials etc. to produce bactericidal and sporicidal materials.

  Cellulose (paper, cotton...) + fluorinated monomers to produce stainless, hydrophobic, anti-adhesive materials etc.

  Cellulose + UV absorbing groups to produce anti-UV textile materials.

Any support + ionic monomers to produce antistatic, reactive, separating materials etc.

Cellulose, polyesters + vinylphosphonate etc. to produce flame retardant textiles.

Any non-harmful support + biocompatible monomers to produce biocompatible materials.

4. Summary

- Thermodynamics of binary polymer mixtures can be described with the help of a lattice model. According to Flory-Huggins, polymer blends have very little mixing entropy, and mixing is determined by energetic factors. Most polymers are indeed immiscible with each other, but there are many exceptions to this rule of thumb because pairwise interaction energy differences are not always repulsive.
- By considering the temperature-dependence of the free energy of mixing, a phase diagram can be constructed to summarize the phase behavior of the mixture, showing regions of stability, instability, and metastability.
- Block copolymers do not macroscopically phase separate but form domains on the scale of tens of nanometers. For monodisperse architectures, phases segregation (order-disorder transition) is accompanied by formation of well-defined periodic structures.