# Polymers in Solution

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Polymers, especially when compared with the monomers from which they are built, have a number of special properties. For example, polymers such as starch and polypropylene oxide are much less soluble in water than their monomers, glucose and propylene oxide. Another observation is that many polymers absorb solvents or water without themselves dissolving. Thus, cotton socks, for instance, absorb water without disintegrating when they are washed in a washing machine. To explain and to be able to describe such properties, this chapter is devoted to a description of the polymeric chain structure and the consequences thereof for polymers in solution. Furthermore, the thermodynamics of polymer solutions are discussed and compared with those of small molecules to develop an understanding of the differences in solubility mentioned above.

## 2.1 Chain Models

The structure of a polymer and the characteristics that can be derived from it can best be visualized by using a chain model. In this model the repeating units are the chain links, which are (in the simplest linear case) connected together to form a chain. In the case of a polymer chain in which all elements are connected in a *trans*-conformation, the simplified image in ◘ Fig. 2.1 emerges.

The "*contour length*," $l_{cont}$—the complete length of a chain with $n$ links of length $l$, including all chain elements— is

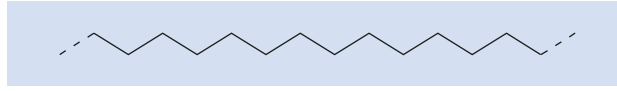
$$l_{cont} = n\,l \tag{2.1}$$

If one considers solely the three most probable conformational possibilities of every $-CH_2-$ entity relative to its direct neighbors, two *gauche*- and one *trans*-conformations, this already gives $3^{n-1}$ different conformations for the complete polymer chain. Only one of these is the *all-trans*-conformation; thus its actual occurrence is highly improbable. Despite this, statistical methods are used to describe the dimensions of polymer chains as realistically as possible and thereby predict their behavior.

The so-called *Gaussian chain* is a random arrangement of the segments following the erratic flight or *random walk* model and assuming free and unimpeded rotation. Every repeat unit is thus connected to the next by an arbitrary angle. ◘ Figure 2.2 shows schematically the basic features of this model.

A statistical treatment is based on the size of the mean end-to-end distance $\vec{R}$.[1] It follows from this that

$$\vec{R} = \sum_{i=1}^{n} \vec{l}_i \tag{2.2}$$



◘ **Fig. 2.1** Model of a polyethylene chain in which the $-CH_2-$ units are symbolized by kinks. The basis of this representation is an *all-trans*-conformation (bond angle = 109.47°)

1 For reasons of consistency with the most popularly used nomenclature, the symbol $R$ is used for this variable; needless to say, it should not be confused with the universal gas constant $R$.

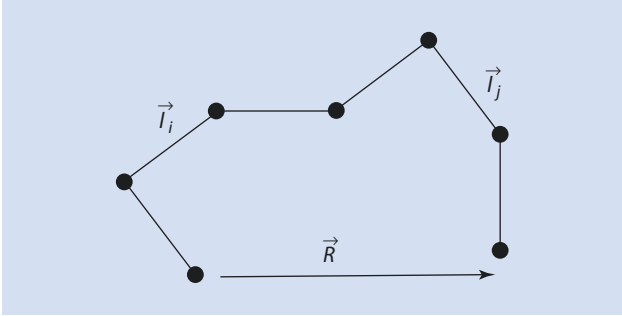



**Fig. 2.2** The Gaussian chain model with different repeating units (e.g., $\vec{l}_i$ and $\vec{l}_j$), which are described by vectors according to their spatial position. $\vec{R}$ is a measure of the distance between the chain ends

If a chain end is randomly placed at the point of origin of a one-dimensional coordinate system, the probability $P(x,n)$ of finding the other end of the chain with $n$ links of the length $l$ at a distance $x$ in the interval $dx$ can be described by a Gaussian distribution. This corresponds to the observation that, in the case of random walk, all directions are equally probable. Thus it holds (without proof) that

$$P(x,n) = \sqrt{\frac{2}{nl^2\pi}} \exp\left(-\frac{x^2}{2nl^2}\right) dx \tag{2.3}$$

Essentially, (2.3) includes the exponential term of a Gauss function as well as a pre-exponential factor. The latter ensures that the integral of this probability distribution is 1 for all values of $x$ because the probability of finding the second chain end somewhere is obviously 1 or 100 %.

In three dimensions, this produces the following result (again without proof):

$$P(x,y,z,n) = \left(\frac{2\pi}{3} nl^2\right)^{-\frac{3}{2}} \exp\left(-\frac{3}{2}\frac{x^2+y^2+z^2}{nl^2}\right) dx \cdot dy \cdot dz \tag{2.4}$$

This expression corresponds to the probability of finding the other chain end in a cubic element of volume $dx \cdot dy \cdot dz$. However, if we observe the model not in the Cartesian system but within spherical coordinates to establish the probability of finding the chain end in a spherical shell of a sphere of thickness $dr$ at a distance $r$ from the center of the sphere (Fig. 2.3), it follows that

$$P(r,n) = \left(\frac{2\pi}{3} nl^2\right)^{-\frac{3}{2}} \exp\left(-\frac{3}{2}\frac{r^2}{nl^2}\right) 4\pi r^2 dr \tag{2.5}$$

To be able to make statistically significant assertions, we calculate (comparable to an error calculation) using the corresponding squared values. This can be visualized by looking at $P(r)dr$ (Fig. 2.4).

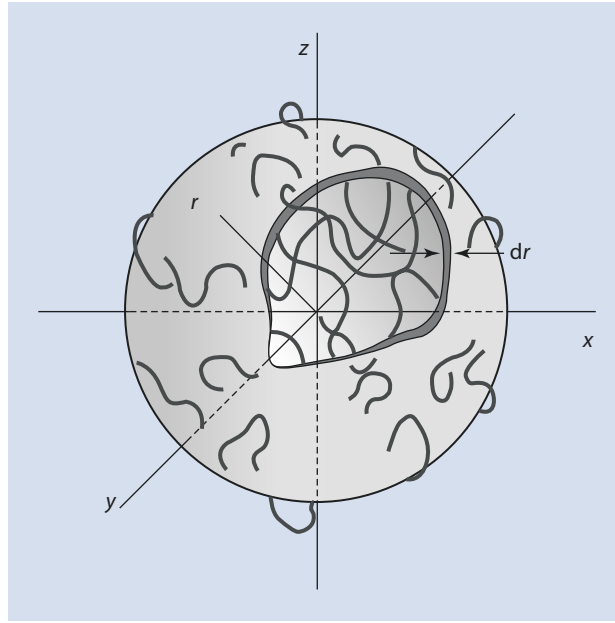



**Fig. 2.3** Spherical shell model of a Gaussian chain

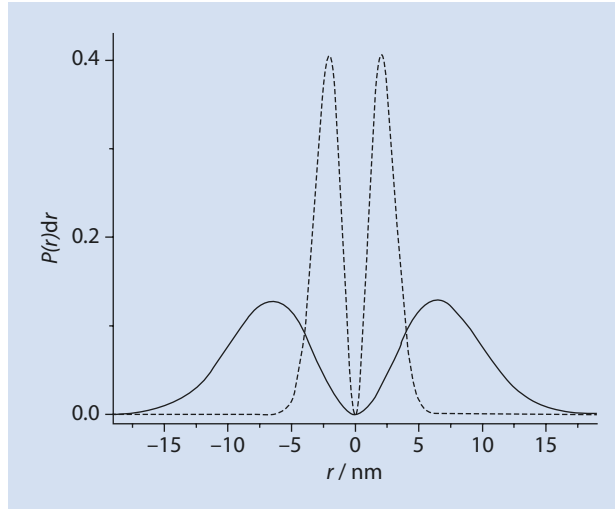



**Fig. 2.4** Representation of $P(r)$ dr *for* $l = 0.25$ nm. (*Dashed line*: $n = 100$, *solid line* $n = 1000$)

In this case, a simple average would yield zero, which of course would not reflect reality, because both chain ends cannot be in the same place—i.e., the origin of the coordinate system—at the same time.

As can be seen in Fig. 2.4, the segment's density tends to zero at the origin. It initially increases outwards before decreasing again at very large distances, a progression that would be intuitively expected.

As the number of chain links $n$ tends to infinity, the mean square end-to-end distance is

$$\left\langle R^2 \right\rangle = \int_0^\infty P(r,n) r^2 dr \tag{2.6}$$

The solution of the integral in (2.6) yields (without proof)

$$\left\langle R^2 \right\rangle = nl^2 \tag{2.7}$$

When $\langle R^2 \rangle$ is compared to the contour length $l_{cont}$, it becomes clear that the coiling of the polymer chain has an enormous effect on the dimensions of the chain. If we consider, for example, a polyethylene chain with a repeat unit length $l = 0.25$ nm and 10,000 units, the contour length, as given by (2.1), $l_{cont} = 2500$ nm, and the mean end-to-end distance according to the *random walk* model, $\sqrt{< R^2 >} = 25$ nm. Thus, $\sqrt{< R^2 >}$ is a factor of 100 shorter than $l_{cont}$.

A more realistic description of a polymer chain compared to that given by a Gaussian chain can be obtained if both the fixed connecting angles and the limited and restricted rotation around the bonds are taken into account. These considerations lead to an expansion of the polymer coil as compared to the Gaussian chain.

If we consider a fixed bond angle $\theta$ for the square of the mean square end-to-end distance in accordance with the so-called *valence bond model* (VBM), it follows (without proof) that

$$\left\langle R^2 \right\rangle_{VBM} = nl^2 \frac{1-\cos\theta}{1+\cos\theta} \tag{2.8}$$

In the case of a carbon–carbon main chain, a bond angle of 109.47° yields

$$\left\langle R^2 \right\rangle_{VBM} = 2nl^2 \tag{2.9}$$

Thus, taking a fixed bond angle into account leads to a doubling of the mean square end-to-end distance. If one also takes into account the restricted rotation at the angle $\Phi$ with non-independent potential, i.e., the preference of *trans* and *gauche* states, one arrives at the so-called *Rotational-Isomeric-State-Model* (*RIS*) (Flory 1953; Painter and Coleman 2009). In this model, the mean square end-to-end distance (without proof) is

$$\left\langle R^2 \right\rangle_{RIS} = nl^2 \left( \frac{1-\cos\theta}{1+\cos\theta} \right) \left( \frac{1+\langle \cos\Phi \rangle}{1-\langle \cos\Phi \rangle} \right) \tag{2.10}$$

Thus, compared to (2.8), taking account of the *trans* and *gauche* "wells of potential," which are expressed by the statistical mean value of the cosine $\Phi$, leads to a further expansion of the chain as compared to the *valence bond model*.

If these differing values of the mean square end-to-end distance are considered in relation to the Gaussian chain, one can derive fundamental information without having to revert to the physically more correct, but mathematically considerably more complex, models. However, with the current models a generally valid description of the dimensions of real polymer chains in undisturbed states is not possible.

An important value is the *characteristic ratio* $c_\infty$, which describes the expansion and therefore the stiffness of the real polymer as compared to the Gaussian chain (2.10). The influence of solvents is not considered and existing interactions are considered to be mutually neutralized (*unimpeded dimensions*). The larger this characteristic ratio (and thus the corresponding square of the mean square end-to-end distance $\langle R^2 \rangle_{real}$ of the real polymer), the more rigid the polymer.

$$\frac{\langle R^2 \rangle_{real}}{n \cdot l^2} \equiv c_\infty \tag{2.11}$$

Of course the assumption of free bond angles makes the Gaussian chain model a gross simplification of real polymers. By avoiding a more detailed structure, the model can serve as a simplification. Where the characteristic ratio is known from experiments, such as size exclusion chromatography (SEC) under $\theta$ conditions (▶ Chap. 3), the model is perfectly adequate to give an approximate description of real polymers. In a development of this model by Kuhn, the length $l_k$ no longer represents that of a repeat unit, but is generally longer. Common to both the real chain and the so-called *Kuhn chain*, which is constructed of $n_k < n$ segments of length $l_k > l$, are the contour length $l_{cont}$ and the real chain end-to-end distance. Figure 2.5 shows the model schematically.

Thus, $l_{cont}$ is given by

$$l_{cont} = n_k \cdot l_k = n \cdot l \tag{2.12}$$

If one considers the real chain and compares the Kuhn model with the Gaussian chain, one obtains

$$\frac{\langle R^2 \rangle_{real}}{n \cdot l^2} = \frac{\langle R^2 \rangle_k}{n \cdot l^2} = \frac{n_k \cdot l_k^2}{n \cdot l^2} = \frac{l_k}{l} \cong c_\infty \tag{2.13}$$

The example of polyethylene ($n > 100$, $l = 0.25$ nm) provides a useful illustration. As a simplification, one assumes that each segment exists independently of its neighboring segment

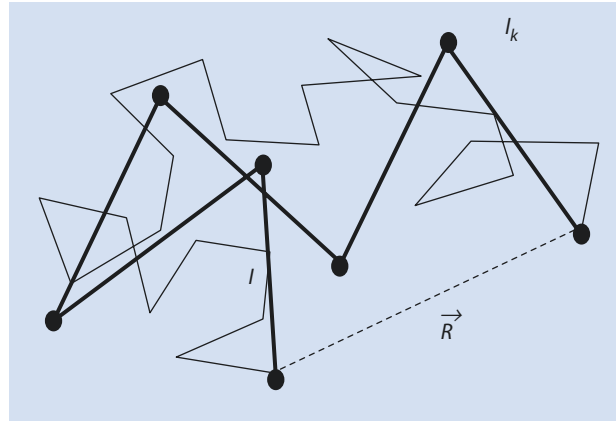



**Fig. 2.5** Schematic representation of the Kuhn model and the corresponding real chain. *Bold* = segment length $l_k$ (Kuhn model), *not bold* = *the elements of the real chain*

in the *gauche* or *trans* state. In this case, the *gauche-trans* energy levels are statistically independent (unconnected) and it follows from theoretical calculations that

$$\frac{\langle R^2 \rangle_{VBM}}{n \cdot l^2} = 3.7 \tag{2.14}$$

However, experiments yield

$$\frac{\langle R^2 \rangle_{k}}{n \cdot l^2} = 6.7 \tag{2.15}$$

Thus, the mutual influence (coupling) of the conformations cannot be ignored. Only a model considering the linked and restricted rotation is capable of describing the expansion of the real polymer coil compared to the Gaussian chain. With (2.13) the Kuhn length $l_k = 1.68$ nm.

In other words, it is possible to calculate the mean square end-to-end distance from the contour length and the Kuhn length directly:

$$\langle R^2 \rangle_k = l_k l_{cont} \tag{2.16}$$

## 2.2 Chain Stiffness

An additional unit of measure for the flexibility of a polymer bundle is the *persistence length* $l_p$. The model describes a chain with an infinite number of bond vectors $\vec{l}_i$, each of identical length. The projection length of each of the bond vectors $\vec{l}_j$ with $j > i$ onto $\vec{l}_i$ is given by the average of all conformations, $l\cos\theta_{i,j}$. This can be graphically interpreted as the portion of all $\vec{l}_j$ that "point" in the direction of $\vec{l}_i$ and can thus be used as a measure of the correlation of the orientation of two independent segments of the polymer chain. Here $\theta_{i,j}$ denotes the angle between the two bond vectors. The so-called *persistence length* is defined as the sum of all the bond vector projections over all conformations on the first vector $\vec{l}_i$:

$$l_p = l \sum_{j=i+1}^{\infty} \langle \cos\theta_{i,j} \rangle \tag{2.17}$$

The initial summands in this expression make a finite contribution to the persistence length. After a certain separation between the bond vectors $\vec{l}_i$ and $\vec{l}_j$ they become independently orientated in space. Thus $\langle \cos\theta_{i,j} \rangle$ converges for these bond vectors to zero and the persistence length becomes a finite value defined by those segments immediately following $\vec{l}_i$. For a stiff polymer, $l_p$ assumes a large value as a result of the considerably restricted rotation. For a statistical coil, $l_p$ has a small value. The persistence length is thus a measure for the stiffness of the coil.

For the limiting case of a bond angle of $\theta = 180°$, the macromolecule forms a straight chain and the mean end-to-end distance is equivalent to the contour length. A mathematical simplification suggests applying the angle complementary to 180°. For $\theta = 180°$ this is $\theta' = 0°$. Although there are real polymers which have a small value for $\theta'$, the angle is always greater than zero. An example of this is a double-strand DNA helix. To describe the characteristics of this chain, considerably fewer and correspondingly longer Kuhn segments would be required than would be necessary for a more flexible polymer.

At this stage, the fundamental difference between the contour length $l_{cont}$ and the persistence length $l_p$ should be noted. The persistence length basically depends on the chain stiffness of the polymer in question. Hence, it is a material characteristic closely associated with the chemical composition of the polymer; it does not depend on the molar mass of the particular chain. For this reason alone is it possible, for example, to define the (single) characteristic persistence length of a polymer such as polyethylene. In contrast to this, the contour length is very heavily dependent on the number of repeat units making up the polymer—as can be immediately seen from (2.1); a doubling of the molar mass leads to a doubling of the contour length. Therefore in specific cases it can be that the persistence length is greater than the contour length for a very stiff polymer with a relatively small molar mass, even if this seems to be in conflict with (2.17) (persistence length as projection of all bond vectors onto the first).

The so-called *wormlike-chain-model* (*WLC*) is a simplified way of considering the chain stiffness of semi-flexible polymers. This mathematical model was first described in 1949 (Kratky and Porod 1949). The persistence length $l_p$ was defined as

$$l_p = \frac{2l}{\theta'^2} \tag{2.18}$$

and the auxiliary parameter $p$ :

$$p \equiv l_p / l_{cont} = \left(2 / n\theta'^2\right) \tag{2.19}$$

This auxiliary parameter allows a dimensionless description. This demonstrated that for the mean square end-to-end distance, it holds (without proof) that

$$\left\langle R^2 \right\rangle_{WLC} = l_{cont}^2 \left[ 2p - \left(\frac{1}{n}\right) - 2p^2 \left(1 - \exp\left(-\frac{1}{p}\right)\right)\right] \tag{2.20}$$

It should be borne in mind that the persistence length is a mathematical paraphrase of the stiffness of the polymer chain. In limiting cases, it tends towards zero (completely flexible chains) or towards infinity (completely stiff rods). Given this, two limiting cases can be distinguished. In the case of extremely stiff chains with a persistence length greater than the contour length, it holds that $p \gg 1$ . As a visual example, one could imagine uncooked spaghetti (which could be even longer without doubling up as a chain does). If we imagine spaghetti of immense length, the description would segue into the second case, as presented below. The exponential function can then be expressed as a Taylor development and ignored after the second term. This gives the following relationship between the end-to-end chain distance and contour length:

$$\left\langle R^2 \right\rangle_{WLC} \approx l_{cont}^2 \left[ 2p - 2p^2 \left(\frac{1}{p} - \frac{1}{2p^2}\right)\right] = l_{cont}^2 \tag{2.21}$$

With this function, stiff chains, for example, rods can be described.

In the second case, we are concerned with molecules that are relatively stiff but have such a large number of segments that the contour length far exceeds the persistence length. An example of this is DNA, mentioned above. DNA is very stiff and has an extremely high contour length. For such molecules $p \ll 1$ which means that $p^2$ is much

smaller than $p$ and, because $n$ is extremely large, $1/n$ is also very small so that (2.20) can be simplified to

$$\left\langle R^2 \right\rangle_{WLC} = 2pl_{cont}^2 = 2l_p l_{cont} \tag{2.22}$$

Making use of the results of the Kuhn chain statistics (2.16) and assuming that $\left\langle R^2 \right\rangle_{WLC} = \left\langle R^2 \right\rangle_k$:

$$l_k = 2l_p \tag{2.23}$$

This restates that the persistence length and the Kuhn length are a measure of the stiffness of polymer chains.

## 2.3 Entropy Elasticity

The Gaussian chain is the (simplified) state of equilibrium for a chain and therefore represents the energy minimum. As a consequence, to expand a Gaussian chain, energy must be introduced. By stretching the chain we bring it closer to the *all-trans*-conformation, which is the most favorable for flexible chains with regard to the enthalpy, but the most unfavorable formation in terms of entropy. As the number of possible conformations is less in stretched states than before, the entropy decreases. If one takes the Gaussian model (with $n$ chain links of length $l$) as a basis, the change in entropy $\Delta S$ during expansion can (without proof) be expressed with the assistance of the mean end-to-end distance $R$ as follows:

$$\Delta S(R) \propto \frac{3}{2} k_B \left(1 - \frac{R^2}{nl^2}\right) \tag{2.24}$$

Herein, $k_B$ denotes Boltzmann's constant. It can be seen that the further the distance $R$ deviates from the result of the Gaussian model, the greater the loss of entropy associated with chain expansion.

With use of the Gibbs–Helmholtz equation

$$\Delta G = \Delta H - T\Delta S, \tag{2.25}$$

it follows that

$$\Delta G(R) - \Delta H \propto -\frac{3}{2} k_B T + \frac{3}{2} k_B T \frac{R^2}{nl^2} \tag{2.26}$$

In practice, it can be assumed, as a reasonable approximation, that the contribution of the change in enthalpy $\Delta H$ to the total free enthalpy $\Delta G$ during the stretching of a polymer chain at room temperature (or above) is considerably less than the value $T \cdot \Delta S$ associated with the change in entropy. As a result, $\Delta H$ can be ignored for the following consideration as a first approximation.

The returning force $F$ of an elongated coil results from the change in the free energy at the absolute temperature $T$ as a function of $R$. Consequently, for small deflections we find that

$$R \ll l_{cont} = n \cdot l;$$
$$F = \frac{\partial \Delta G}{\partial R} \propto \frac{3k_B T}{nl^2} R \tag{2.27}$$

The resilience of a polymer chain, which in macroscopic terms corresponds to the resistance of a polymeric material to deformation, depends on the entropy of the chain and is thus proportional to the mean end-to-end distance between chain ends.

## 2.4 Thermodynamics of Polymer Solutions

In chemical terms, a polymer melt is composed of identically structured molecules. Moreover, density fluctuations are small enough to be ignored. The chemical environment a molecule "sees" is therefore the same throughout the whole melt. Such a situation can be described by an averaged, so-called *mean field*. In this scenario, the dimensions of the polymer are not affected by interactions, for example, with neighboring, chemically dissimilar molecules.

In contrast, in dilute polymer solutions, the density, chemistry, and especially the chemical potential of the system fluctuate as a function of location. In such dilute solutions, the polymer coils are separated by "empty," solvent filled spaces. Moreover, as elucidated in ▶ Sect. 2.1, the segment density within the polymer coils is not homogeneously distributed. In contrast to the melt, a "non-mean field" state prevails. As a result, interactions are present that can influence the conformation of the polymer. To understand the behavior of polymer solutions, it is necessary to consider their thermodynamics.

A polymer solution consists of the dissolved polymer and at least one solvent. Thus, in the simplest case we are dealing with a two-component system. A system consisting of a greater number of components might be a solvent mixture or a solution of more than one polymer.

### 2.4.1 Ideal and Real Solutions

The characteristic ratio has already been introduced in ▶ Sect. 2.1. It can also be called the ratio of the *undisturbed dimension* of a real polymer coil in relation to the ideal Gaussian chain. The undisturbed dimension is derived directly from the molecular structure of the polymer. This state is the one most probable in the melt, in which the polymer molecules are only surrounded by essentially similar molecules. If, however, the polymer is dissolved in a solution, additional interactions are present that can influence its shape. In a good solvent, the interactions between the polymer and the solvent are favored over the interactions of the individual components. As a result, the polymer coil expands. In contrast, in a poor solvent the coil collapses. The transition from a good to a poor solvent, a so-called *θ-solvent,* presents a special case. In such solvents the interactions between the polymer segments are equally prevalent as those between the polymer and solvent molecules. For any one set of substances this state is normally only present at a specific temperature, the so-called *θ-temperature*. Details of this are discussed further below.

The thermodynamic properties of a polymer solution are determined by the interaction between the solvent and the dissolved substance, the so-called solvent quality. The solvent quality varies considerably for the same solvent, depending on the dissolved

polymer. For example, water is a very good solvent for polyethylene oxide (PEO), whereas polystyrene is barely soluble in water. To understand the thermodynamics of polymer solutions, just as with small molecule solutions, one needs to consider the Gibbs–Helmholtz equation:

$$\Delta G^m = \Delta H^m - T\Delta S^m \tag{2.28}$$

Here $\Delta G$ is the Gibbs free enthalpy, $\Delta H$ the enthalpy, $T$ the absolute temperature, and $\Delta S$ the entropy. The index $m$ refers to the respective values for the mixture.

For small molecule mixtures, depending on the quality of the solvent, the following limiting cases can be identified.

### Ideal Solution

The special case of an ideal solution arises if the process of mixing with the substance being dissolved does not lead to any change in enthalpy (heat) and the entropy of the mixture is expressible using the simple statistical approach of the so-called *ideal entropy of mixing*. The latter is derived in detail further below. Thus

$$\Delta H^m = 0 \quad \text{and} \tag{2.29}$$

$$\Delta S^m = \Delta S^m_{ideal} \tag{2.30}$$

### Athermal Solution

During the production of an athermal solution, no heat of reaction is observed ($\Delta H^m = 0$). However, the entropy change deviates from the statistically derived ideal entropy of mixing $\Delta S^m_{ideal}$, the deviation being denoted by $\Delta S^m_{excess}$. Thus

$$\Delta H^m = 0 \quad \text{and} \tag{2.31}$$

$$\Delta S^m = \Delta S^m_{ideal} + \Delta S^m_{excess} \tag{2.32}$$

### Regular Solution

The regular solution is associated with a heat of solution $\Delta H^m_{excess}$, but the change in entropy is ideal:

$$\Delta H^m = \Delta H^m_{excess} \quad \text{and} \tag{2.33}$$

$$\Delta S^m = \Delta S^m_{ideal} \tag{2.34}$$

### Real (Irregular) Solution

Finally, for real, sometimes called irregular solutions, a heat of solution and a deviation from the ideal entropy of mixing can be observed:

$$\Delta H^m = \Delta H^m_{excess} \quad \text{and} \tag{2.35}$$

$$\Delta S^m = \Delta S^m_{ideal} + \Delta S^m_{excess} \tag{2.36}$$

## θ Conditions

In this special case, the mixture behaves in a pseudo-ideal fashion. Under these conditions, the free enthalpy of mixing is zero; the enthalpy of mixing and the term including the temperature and the entropy of mixing are equal:

$$\Delta H^s = T\Delta S^m \tag{2.37}$$

The effect that the solvent quality has on the polymer coil's dimensions is shown schematically in Fig. 2.6.

In the following section we concern ourselves with describing those regular solutions which are especially important in practice.

### 2.4.1.1 Solutions of Lower Molecular Substances

A lattice model is suitable for describing a solution of a small molecule (Fig. 2.7).

If it is assumed that the respective values of molecular and cellular size are identical, the respective volume fraction $\varphi_i$ is equal to the corresponding mole fraction, given by the respective number $N_i$:

$$\varphi_i = \frac{V_i}{V_1 + V_2} = \frac{N_i}{N_1 + N_2} \tag{2.38}$$

Here the index $i$ can either describe the solvent (index 1) or solute (index 2). For the case shown in Fig. 2.7, the ideal entropy of mixing can be determined from the number of possible combinations of positions $W$:

$$\Delta S^m_{ideal} = k_B \ln W \tag{2.39}$$

Statistically, $W$ amounts to (without proof)

$$W = \frac{N!}{N_1!\,N_2!} \tag{2.40}$$

Because the sum of $N$ is determined by $N_1$ and $N_2$, with the aid of the Sterling approximation

$$\ln N! \approx N \ln N - N \tag{2.41}$$

and the following simplification can be made:

$$\Delta S^m_{ideal} = k_B N \left( \ln N - \frac{N_1}{N} \ln N_1 - \frac{N_2}{N} \ln N_2 \right) \tag{2.42}$$

For 1 mol (corresponds to $N_A$ molecules, where $N_A$ is Avogadro constant) with the introduction of the volume fraction and the universal gas constant $R = k_B N_A$, it follows that

$$\Delta S^m_{ideal} = R \left( \ln N - \frac{\varphi_1 N}{N} \ln \varphi_1 N - \frac{\varphi_2 N}{N} \ln \varphi_2 N \right) \tag{2.43}$$

$$\Delta S^m_{ideal} = R \left( \ln N - \varphi_1 \ln \varphi_1 - \varphi_1 \ln N - \varphi_2 \ln \varphi_2 - \varphi_2 \ln N \right) \tag{2.44}$$

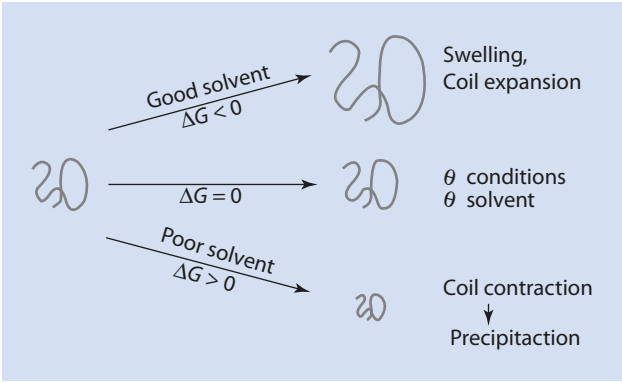



**Fig. 2.6** Schematic representation of polymer coils in solvents of different quality

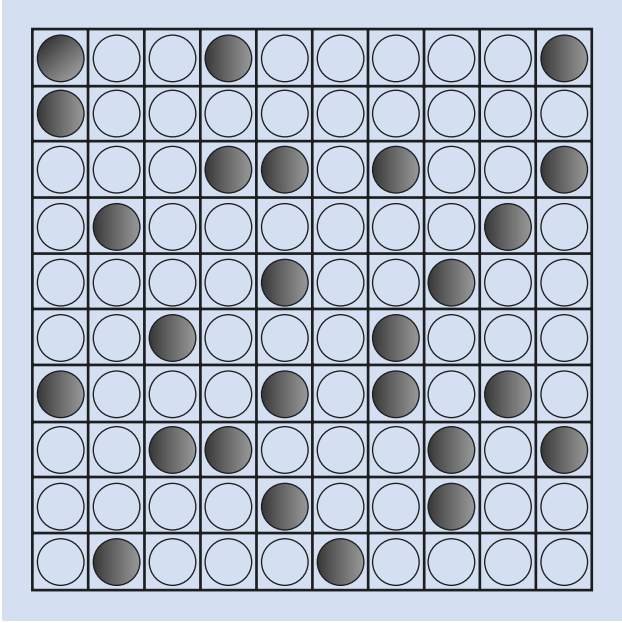


**Fig. 2.7** Lattice model to describe a solution of a solute (*dark points*) in a solvent (*light points*). Apart from the contents the lattice cells are identical

Because the sum of the volume fractions equals 1:

$$\Delta S^{m}_{ideal} = -R\left(\varphi_1 \ln \varphi_1 + \varphi_2 \ln \varphi_2\right) \tag{2.45}$$

Furthermore, because $\varphi_1$ and $\varphi_2$ are always less than 1 for mixtures, the ideal entropy of mixing is always positive and the entropy of mixing always favors the mixture of substances. This should be obvious by considering entropy as a measure of the disorder of a system).

To calculate enthalpies, we take account of the pair-interactions $W_{ij}$ between the neighboring cells in the lattice. To create two contacts between molecules 1 and 2 (with the corresponding enthalpy of interaction $W_{12}$), the interactions between a pair of solvent molecules ($\rightarrow W_{11}$) and a pair of solute molecules ($\rightarrow W_{22}$) must be ruptured. The enthalpy change for this process is given by

$$\Delta W = 2W_{12} - \left(W_{11} + W_{22}\right) \tag{2.46}$$



The total number of contacts $N_{12}$ between solvent and solute in the lattice can be obtained by considering the coordination number $z$, which is given by the number of the neighboring lattice cells:

$$N_{12} = N\varphi_1\varphi_2 z \tag{2.47}$$

Thus, the total enthalpy of mixing for the mixture is given by

$$\Delta H^m = \frac{z}{2} N\varphi_1\varphi_2 \Delta W \tag{2.48}$$

The factor 1/2 results from the definition of $\Delta W$ (in relation to two interaction contacts). This expression can be simplified by introducing the *Flory–Huggins interaction parameter* $\chi$. From the definition of this parameter

$$\chi = \frac{z}{2k_B T}\Delta W, \tag{2.49}$$

it follows for the molar enthalpy of mixing:

$$\Delta H^m = RT \cdot \varphi_1\varphi_2\chi \tag{2.50}$$

Thus, positive values for $\chi$ indicate an endotherm (= unfavorable) interaction between solvent and solute.

With the aid of (2.33), the free enthalpy of mixing $\Delta G^m$ can be formulated as

$$\Delta G^m = RT\left(\underbrace{\varphi_1 \ln\varphi_1 + \varphi_2 \ln\varphi_2}_{\textit{Entropy term}} + \underbrace{\varphi_1\varphi_2\chi}_{\textit{Enthalpy term}}\right) \tag{2.51}$$

The variation of $\Delta G^m$ with the volume fraction of one component is symmetrical over the composition of the system (Fig. 2.8), i.e., changing the indices for the solute and solvent does not change (2.51).

Figure 2.8 shows plots of the free enthalpy of mixing as a function of the composition for various values of $\chi$.

From Fig. 2.8 it can be deduced that mixtures with smaller values of $\chi$ are stable, because for small values of $\chi$ the free enthalpy of the mixing is always less than the free enthalpy of the pure components. That is, mixing the components leads to a reduction of the free enthalpy and is thus energetically favorable. This becomes obvious by considering that large, positive values of $\chi$ would indicate a strongly endothermic mixing process.

For smaller values of $\chi$, the free enthalpy of mixing is always negative. For $\chi > 2$ the free enthalpy of mixing goes through a maximum and the curve forms a "hump" for solutions of equal volume fractions. For such solutions there are alternative compositions to the left and the right of this maximum with lower energy levels, and such systems begin to separate in the range of equal volume fraction compositions—the systems are unstable. This effect increases with increasing values of $\chi$.

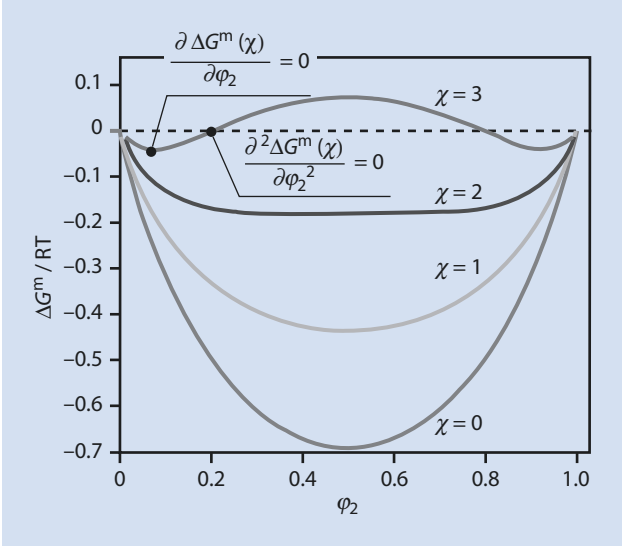



**Fig. 2.8** Plot of the free enthalpy of mixing as a function of the composition for various values of the Flory–Huggins

If one observes, for example, a system at $\varphi_2 = 0.5$ for $\chi = 3$, a separation takes place into two phases with $\varphi_2 = 0.07$ and $\varphi_2 = 0.93$ corresponding to the minima of the energy curve. A special case can be observed for mixtures that are between the minimum and the inflexion point of the free enthalpy curve. Because the curve here also increases to the left, these systems are *metastable* and additional (activation) energy is required to induce the process of phase separation. This phenomenon can be compared with the processes of nucleation and growth during crystallization.

The influence $\chi$ has on the stability limits, stable–metastable–unstable, can be directly determined by plotting $\Delta G^m$ as a function $\varphi$ for different values of $\chi$ and determining the positions of the minima and inflection points. To this end, the minima and inflexion points of the free enthalpy curves in Fig. 2.8 are joined for different values of $\chi$ and transposed to give Fig. 2.9.

The transposition of the minima results in the so-called *binodal*, which separates the stable area from the metastable one. The transposition of the inflexion points yields the so-called *spinodal,* which separates the metastable from the unstable area. The critical point is the point where binodal and spinodal curves converge.

### 2.4.1.2 Polymer Solutions

If one considers polymer solutions, the description in the lattice model according to Flory and Huggins initially changes because monomers are linked together to form the polymer chains (Fig. 2.10).

The mathematical description of polymer solutions in analogy to that for small molecules is given in (2.51), analogously to the lower molecular substances discussed so far. For the free enthalpy of mixing $\Delta G^m$, it holds without proof:

$$\Delta G^m = RT \left( \underbrace{\varphi_1 \ln \varphi_1 + \frac{\varphi_2}{X_N} \ln \varphi_2}_{\text{Entropy term}} + \underbrace{\varphi_1 \varphi_2 \chi}_{\text{Enthalpy term}} \right) \tag{2.52}$$

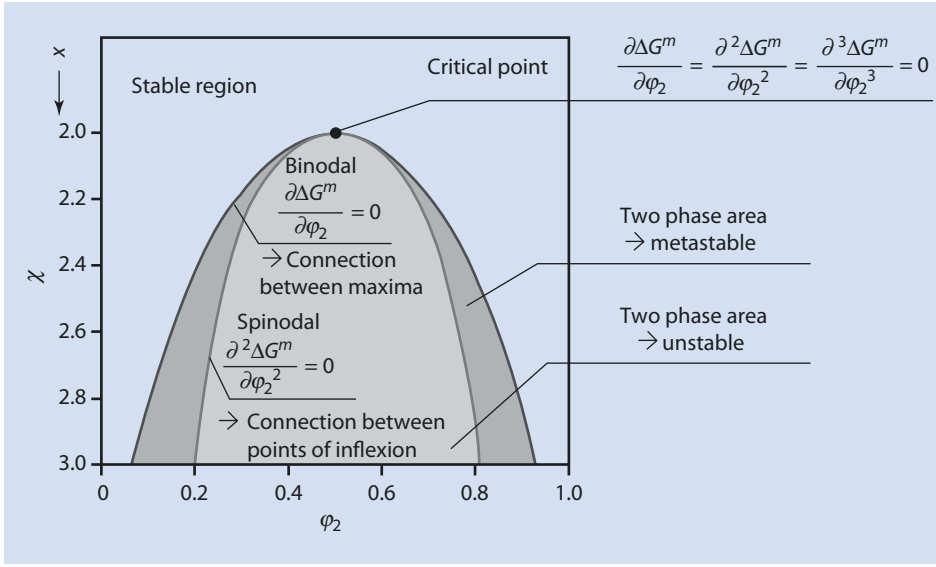



**Fig. 2.9** Binodal and spinodal curves for small molecule mixtures

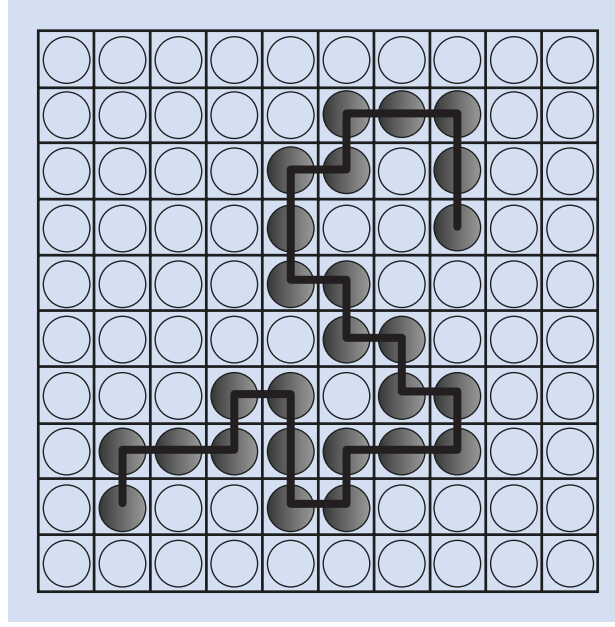


**Fig. 2.10** Lattice model representing a solution of a polymer (*dark circles*) in a solvent (*light circles*). Apart from their contents the lattice cells are identical

In this model, $X_N$ denotes the relation of the size of the polymer molecule to that of the solvent molecule. Assuming that the solvent molecules occupy the same volume as the repeat units in the polymer, $X_N$ corresponds to the degree of polymerization of the polymer being studied.

It is striking that only the entropy term is different for polymer solutions (cf. (2.51)). Descriptively, the entropy gain is lower when diluting a polymer solution than when diluting

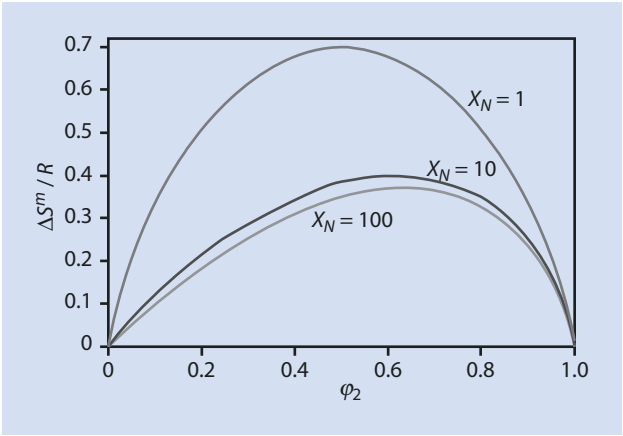



**Fig. 2.11** Entropy of mixing as a function of solution composition for polymer solutes of different chain lengths

a corresponding amount of a small molecule solution because the polymer's building blocks cannot arbitrarily spread themselves over the lattice cells. This means that, compared to a small molecule solution, the dissolution of a polymer is always less favorable with respect to its entropy because of its smaller entropy of mixing whereas the enthalpy of mixing does not change considerably to a first approximation (i.e., for regular solutions) whether it is a small molecule or a polymer being dissolved.

Figure 2.11 shows the curve of the entropy of mixing as a function of solution composition for polymer solutes of different chain lengths.

In contrast to the corresponding curves for solutions of small molecules, (2.52) is no longer symmetrical with respect to the two components; i.e., exchanging the component indices would produce a different and new equation. This is also reflected in Fig. 2.11. The curves are no longer symmetrical about a vertical mirror axis running through a 1:1 mixture and the maximum shifts to higher polymer volume fractions for $X_N > 1$ as the size of the polymer increases. The forms of the curves of the free enthalpy of mixing as a function of $\varphi_2$ for different values of $\chi$ are shown in Fig. 2.12

As in Fig. 2.8, the curves of $\Delta G^m$ for large values of $\chi$ have 2 maxima. However, the minimum at low polymer concentration (small value of $\varphi_2$) is only weakly developed (see insert in Fig. 2.12). The curves in Fig. 2.12, in contrast to those in Fig. 2.8, are also unsymmetrical.

If, in analogy to Fig. 2.9, the binodals for various chain lengths are extrapolated, Fig. 2.13 can be obtained.

From this representation a critical point can be recognized—that the composition at which a miscibility gap is observed for the first time shifts to ever smaller polymer concentrations as the degree of polymerization increases. Moreover, the miscibility gap approaches a critical $\chi$-parameter of $\chi_c = 0.5$. This has two significant implications.

The curves in Fig. 2.13 document that polymers of greater molar mass dissolve less easily than those of smaller molar mass; the solubility of polymers decreases with increasing chain length. The miscibility gap broadens and starts at lower values of $\chi$. For polymers with very high molar mass, a miscibility gap is already evident at a $\chi$-parameter value of 0.5. For such polymers the required entropy of mixing even a much smaller (unfavorable) enthalpy of mixing is necessary to compensate for the reduced (favorable) entropy of mixing and thus to trigger phase separation. The reason for the decreasing solubility of polymers as their degree of polymerization increases is the *entropy* of the system.

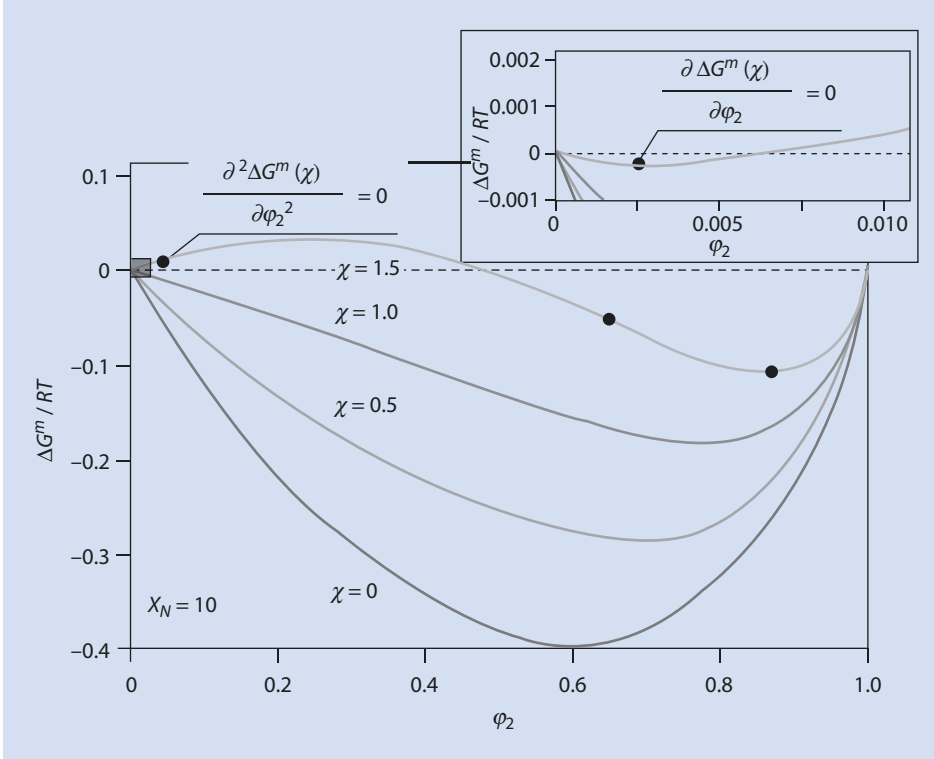



**Fig. 2.12** Curves of the free enthalpy of mixing a polymer and a solvent as a function of $\varphi_2$ for different values of $\chi$ at length $\chi_N = 10$

Furthermore, it follows from this that at high degrees of polymerization the separation leads to a solvent swollen polymer gel and an almost polymer-free solvent phase. Take, for example, a chain with a degree of polymerization of 1000 (we are considering a single lattice cell!) and an interaction parameter $\chi$ of 1. In Fig. 2.13 a straight line for $\chi = 1$ parallel to the x-axis intersects the binodal almost at the ordinate ($\varphi_2 = 0$) and again at $\varphi_2$ of ca. 0.5. This implies that such a mixture separates into two phases, one containing polymer soaked with 50% solvent (in reality a polymer gel) and the other an almost polymer-free solvent phase. With the aid of the asymmetry of the curves, this explains why some polymers absorb large quantities of a solvent without dissolving—think of cotton socks in the washing machine.

For a system with $X_N = 100$ at $\chi = 1.0$ and a mid-range composition of $\varphi_2 = 0.2$, the phase separation results in two phases with polymer volume fractions of $\varphi_2 = 0.01$ and $\varphi_2 = 0.5$, respectively (Fig. 2.13). From the mass balance it is clear that the volumes of the two phases are not equal. The first phase (containing very little polymer) fills approx. 61% of the total system volume whereas the polymer-rich phase occupies the remaining 39%. These figures are obtained from the "difference" between the resulting phase compositions and the original composition, $\varphi_2 = 0.2$. This can be generalized: the phases whose composition after phase separation is most similar to the overall composition occupy the largest volume. The figures of 61 % and 39 % in our example can be calculated from the difference

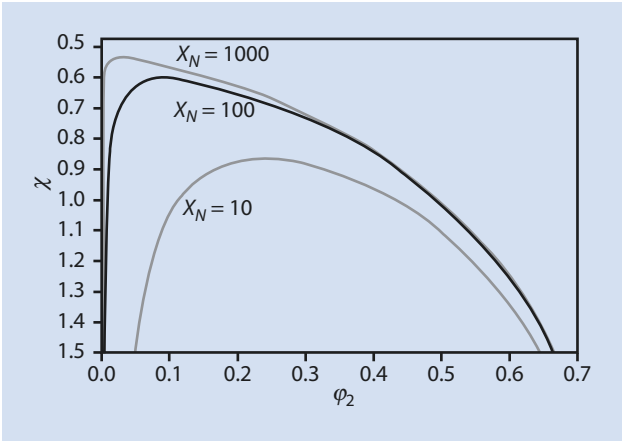



**Fig. 2.13** Binodal curves for solutions of polymers with different chain lengths

between the phase composition and the overall composition ($\Delta\varphi_2 = 0.2 - 0.01 = 0.19$ or $0.5 - 0.2 = 0.3$) relative to the difference between the compositions of the two phases ($\Delta\varphi_2 = 0.5 - 0.01 = 0.49$). Because of the formal analogy to the principle governing mechanical levers, this rule of separation is also referred to as the lever rule.

The Flory–Huggins interaction parameter is a central measure for understanding the solubility of a polymer in a specific solvent. A negative interaction parameter indicates that the polymer and the solvent molecules attract each other to a greater extent than they attract their own kind. The polymer dissolves easily. On account of the good solvation, the polymer coil expands compared to the undissolved state.

An interaction parameter of $\chi = 0$ corresponds to an athermal solution. Graphically speaking, this means that all the interactions taking place in the medium are equal, and it does not matter for the enthalpy of the system whether the interacting neighbors are solvent molecules or polymer segments.

When the Flory–Huggins interaction parameter becomes positive, the enthalpy favors phase separation rather than solution. If, however, a degree of miscibility remains, this is because of the contribution from the entropy of the system. As the entropy contributions in polymer systems are much smaller than those with small molecule solutes, even a slightly positive (unfavorable) enthalpy of mixing suffices to prevent the polymer from dissolving. The properties of polymer solutions are therefore strongly dependent on the value of the interaction parameter $\chi$.

If the interaction parameter has a value greater than 0.5 (for extremely high molar masses), the polymer becomes more compact in the solution. The reason for this is a net rejection between polymer and solvent molecules. The limiting case, $\chi = 0.5$, for polymers with a high degree of polymerization reflects the transition between a homogeneous mixture and separation into two phases. As the interaction parameter increases, attraction between polymer and solvent is reduced, interaction becomes more repulsive in nature, and the polymer precipitates.

Additionally, for $\chi = 0.5$ (for the limiting case of infinite molar mass) there is a special case. As mentioned above, this is the value of $\chi$ at which a miscibility gap is observed for the very first time. At this point, the contributions from the enthalpy and entropy of mixing compensate each other and the solution acts as an ideal solution, i.e., *quasi-ideal*. As already stated, this condition is referred to as the $\theta$ state.

If we compare this to the ideal solution ($\Delta H^m = 0$ and $\Delta S^m = \Delta S^m_{ideal}$), the difference lies in the fact that $\Delta H^m$ is not zero and $\Delta S^m$ also deviates from $\Delta S^m_{ideal}$, but both terms simply compensate each other.

Because the free enthalpy of mixing depends on the temperature according to the Gibbs–Helmholtz equation (2.28), $\Delta H^m$ and $\Delta S^m_{excess}$ usually only compensate each other at a single temperature. This is referred to as the $\theta$-temperature. From (2.28), conditions can be found for instances where $\Delta H^m$ and $\Delta S^m$ differ from zero and $\Delta S^m_{ideal}$, respectively, usually by varying the temperature, and where the solution behaves in a quasi-ideal manner. These conditions are referred to as $\theta$ conditions.

The solubility of a polymer in a solvent therefore depends on the temperature. If a single (homogeneously mixed) phase only exists above a certain temperature, this is referred to as an *upper critical solution temperature* (UCST). Here the separation below the UCST is an enthalpy-driven process—at lower temperatures the contribution of the enthalpy of mixing to the free enthalpy of mixing is greater than the effect of entropy (2.28).

However, if a solution is only thermodynamically stable below a certain temperature, the separation that occurs at this temperature must, by analogy, be driven by entropy. When a thermodynamically stable phase of the polymer–solvent-mixture occurs below a critical temperature, this is referred to as the LCST (*lower critical solution temperature*). This temperature denotes the maximum temperature at which the polymer still dissolves.

Formally, this behavior can be explained by interpreting the Gibbs–Helmholtz equation and considering the signs of the enthalpy and entropy terms. Assuming a negative enthalpy of mixing and a normal, positive entropy of mixing, the solution is completely miscible at all temperatures. An LCST occurs when the entropy and enthalpy of mixing take on negative values. As previously stated, because the entropy of mixing is usually positive, this case is rare and is only observed for a few polymers. If the signs of both the entropy and enthalpy of mixing are positive, the system has a UCST. This is often the case in reality. If the enthalpy of mixing is positive and the entropy of mixing negative, the system is not miscible at any temperature.

For real mixtures the situation is not so trivial, as both enthalpy and entropy of mixing are not monotonically dependent on the temperature. A detailed investigation shows that all polymer–solvent mixtures should display a UCST as well as an LCST. However, these are not always observable by experiment. This can often be explained by the UCST and LCST occurring at temperatures above or below the melting or the boiling point of the solvent.

The theory discussed here can be further modified by taking the temperature dependence of $\chi$ and other possible influences into account. Such refinements are not included in the present introductory description of the subject.

An approach comparable to the Flory–Huggins model for describing the characteristics of solutions is offered by the *Hildebrand solubility parameter.* This is based on a consideration of *coherence energy densities*, which are not discussed further here (Hildebrand and Scott 1950).

Finally, a few limitations of the Flory–Huggins-model are briefly discussed:

- The lattice model assumes that both the mixture's components (solvent and repeat unit) are of the same size and that the overall volume is composed additively from both components; i.e., the mixing process does not lead to a volume contraction or expansion.

- The model only takes account of combinatory entropy. It is based on a statistical mixture of the chains and segments. This makes sense for concentrated solutions but poses difficulties in the case of dilute solutions.
- Likewise, the model only accounts for non-polar molecules; the influence of, for example, hydrogen bonding between the polymer and the solvent is not considered.

In spite of these limitations, the Flory–Huggins theory serves as an excellent basis for a semi-quantitative understanding of the theory of polymer solutions. In detail, this subject is extremely complex.

The Flory–Huggins parameter can be determined by using various experimental methods (► Sect. 3.2.4). Such methods include osmosis as well as the enthalpy of vaporization (making use of solubility parameters) and group contribution calculations based on the results. Because the measurement of the heat of vaporization of a polymer is impractical, swelling experiments are an alternative which is noted here. The reduced solubility of polymers compared to the monomers from which the polymers are composed results from an entropy effect. Knowing this, it is intuitive that the entropy of mixing of two polymers is again considerably reduced. This leads to the important realization that two polymers are generally immiscible.

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