

Polymer Science 2024

Course Notes of Chapter 3.1

Table of Contents

1. Introduction: Conformations in the Condensed State.....	1
2. Macromolecules in the Condensed State	2
2.1 Forces Between Molecules and Binding Energies	2
2.2 Cohesive Energy, E_{coh} , and its Importance.....	2
2.3 Relationship Between E_{coh} and Solubility	3
3. Summary	5

1. Introduction: Conformations in the Condensed State

This week we are dealing with the **condensed state**. We will start with solutions, and then continue with **amorphous polymers** which, to be useful as structural materials, must generally be in a **glassy state**.

In the previous chapter 2 of our class, we have considered isolated chains by a theoretical description of chain conformations. While this is relevant for measuring techniques of the "size" of polymer chains that involve a solvent, such as GPC, we will see that it is indeed difficult or even impossible to obtain a polymer of high molar mass in the form of a gas. "**Condensed state**" refers to any state where molecules are in intimate contact, whether in the form of a liquid or a crystalline or amorphous solid, or in the form of an elastomer (a solid in the strict sense of the definition of an amorphous solid (see later Chapter 3.2), which, however, also has certain characteristics of a liquid). A gas or a plasma are therefore not condensed systems. On the other hand, a solution is a condensed system, but since the molecules of a polymer in very dilute solution are far apart from each other, certain aspects of their behavior can be considered to be characteristic of isolated chains. However, this behavior depends on the affinity of the solvent for the polymer. Paradoxically, as discussed at the end of Chapter 2, it is only when a polymer chain is in intimate contact with other chains to which it is chemically identical that we find the ideal conformations of an isolated chain.

2. Macromolecules in the Condensed State

2.1 Forces Between Molecules and Binding Energies

In the condensed state, we can distinguish different forces between macromolecules. We can include the forces which connect the atoms or the monomers within a chain, which are of covalent nature in a synthetic polymer, and associated with energies of the order of a few hundred kJ/mol, i.e. about **420 kJ/mol for a CH bond and about 350 kJ/mol for a CC bond**. There are still the **secondary interactions**, i.e. **non-covalent interactions**, such as van der Waals forces, hydrogen bonds etc. **The bond energy associated with secondary interactions between two repeating units of a typical polymer will be of the order of 10 kJ/mol**. Finally, if the molecules get too close, they experience repulsive forces. Two molecules cannot occupy the same space at the same time (Pauli exclusion principle)!

This explains why it is difficult to obtain a polymer in the gaseous state. The energy required to separate the molecules of a polymer in a condensed state, i.e. to break all secondary bonds, is on the order of n times 10 kJ/mol if the polymer contains n repeating units, or 10^3 kJ/mol already for a moderate polymer size containing only 100 repeating units. If we provided this energy by adding heat, we would have more than enough energy to break the covalent bonds (380 to 420 kJ/mol) before reaching a value high enough to evaporate the polymer.

2.2 Cohesive Energy, E_{coh} , and its Importance

The energy required to separate molecules of a liquid or a solid is called the cohesive energy:

$$E_{coh} = \Delta H_{vap} - RT \quad (1)$$

Here, ΔH_{vap} is the enthalpy of evaporation and RT takes the entropy of the vapor into account. In Slides 102-109 you see a list of the different types of secondary interactions including dipolar interactions, hydrogen bonds and the dispersion forces that are usually found in synthetic polymers. Note that **the secondary binding energy depends in all these cases on r^{-6}** where r is the separation between molecules. We know less well the shape of the repulsion energy, but, in a first approximation, we assume that it varies like r^{-12} , which gives us the **Lennard-Jones potential** (per mol):

$$U = -Ar^{-6} + Br^{-12} \quad (2)$$

sketched in Slide 110, where A and B are constants. The molecules of a liquid or a solid will then seek to adopt a r_0 separation which minimizes U . Thus:

$$\frac{dU}{dr} = 6Ar^{-7} - 12Br^{-13} = 0$$

$$\Rightarrow r_o = \sqrt[6]{\frac{2B}{A}}$$

and
$$E_{coh} \equiv U(r_o) = -A \left(\frac{2B}{A} \right)^{-1} + B \left(\frac{2B}{A} \right)^{-2} \quad (3).$$

It is clear that this energy is very important for the behavior of a condensed polymer (see Slide 111). For example, we can “easily” show (Exercise) that the bulk modulus is

$$K \equiv -V_o \left. \frac{d^2 U}{dV^2} \right|_{V=V_o} = \frac{8E_{coh}}{V_o} \quad (4),$$

where $V \cong r^2$ is the molar volume of a segment of the polymer (note already that this quantity does not strongly depend on temperature!) and E_{coh} is the cohesive energy of a mol of segments.¹ Thus, even if we cannot directly measure E_{coh} for a polymer by evaporating it (we can do it for a small molecule) and if we do not know *a priori* the constants A and B , we can associate it with measurable quantities such as K .

2.3 Relationship Between E_{coh} and Solubility

We have seen that we cannot evaporate a polymer by adding heat without breaking its covalent bonds, but that we can separate the molecules by dissolving it. However, the energy of dissolution is not E_{coh} , because one must take the interactions between the polymer and the solvent into account (Slide 115). A solution is only a mixture of two or more different substances (which does not need to be liquid). We are going to mix a substance composed of blue balls with a substance composed of gray balls of identical size. Isolating one mole of gray balls costs an energy of E_{coh}^2 and leaves one mole of “holes” behind. It costs an energy of E_{coh}^1 to make “holes” in the substance composed of blue balls. But if we put the gray balls in these holes, and the blue balls in the holes left by the gray balls, the total energy balance becomes

$$\Delta H_{mix} = E_{coh}^1 + E_{coh}^2 - 2E_{coh}^{12} \quad (5),$$

where it is assumed that the molar interaction energy between the gray and blue balls is the geometric mean of E_{coh} of the pure substances

¹ The choice of segment is somewhat arbitrary here, but it does not make sense to set E_{coh} for an entire chain since its value would then depend on the chain length.

$$E_{coh}^{12} \approx \sqrt{E_{coh}^1 E_{coh}^2} \quad (6),$$

$$\text{So, } \Delta H_{mix} = \left(\sqrt{E_{coh}^1} + \sqrt{E_{coh}^2} \right)^2 \equiv V_o (\delta_1 - \delta_2)^2 \quad (7),$$

where $\delta = \sqrt{E_{coh}/V_o}$ is the **solubility parameter**, and V_o is the minimum molar volume. As we can evaporate the small molecules of the solvents, we can estimate δ directly from E_{coh} . To do the same for a polymer segment having the same molar volume V_o , one could qualitatively estimate the solubility by comparing δ of a potential solvent and the polymer segments based on Equation 7 - *a priori* if ΔH_{mix} is low, i.e. if the δ are close, the enthalpy cost to make the mixture will be low and the dissolution will be favorable, even if we do not take the entropic contributions to the free energy of dissolution into account.²

In practice, instead of comparing single values of δ , we consider separately the contributions of van der Waals (dispersion) forces, δ_{vdV} , dipolar interactions, δ_d , and hydrogen bonds, δ_h :

$$\delta^2 = \delta_{vdV}^2 + \delta_d^2 + \delta_h^2 \quad (8).$$

$$\Delta H_{mix} = V_o (\delta_{vdV1} - \delta_{vdV2})^2 + V_o (\delta_{d1} - \delta_{d2})^2 + V_o (\delta_{h1} - \delta_{h2})^2$$

It remains to be seen how to obtain the values of the different δ for a polymer and whether a polymer is soluble in a given solvent. However, we will turn the problem upside down as shown in slide 117, by trying to dissolve the polymer in many different solvents in which we know its solubility. We draw a point for each solvent on a three-dimensional graph whose axes correspond to the different components of δ , and we indicate whether the polymer in question is more or less soluble in this solvent. It is then assumed that the values of δ for the polymer correspond to the center of a sphere which groups the points associated with the best solvents.

To do what? Because **the solubility of polymers is very important for their applications** (Slide 118) and because **this allows us to systematically estimate E_{coh}** and thus the physical properties, such as K , which depend on it. As shown in Slide 118, this works quite well given the approximations inherent in this approach.

² The entropic contributions are indeed very important (cf. the theory of Flory-Huggins, Chapter 5) because our simple approach implies that ΔH is always positive unless the δ are identical, and a positive free energy of dissolution would imply that the solution is always unstable. In reality, ΔE can be negative if there are strong specific interactions between the polymer and the solvent (which can also be another polymer).

3. Summary

- In the condensed state (melt, solid) interchain interactions are dominated by Van der Waals forces. These are relatively weak, make processing easy, but are still strong enough to prevent e.g. evaporation.
- The cohesive energy is the energy required to separate molecules, but cannot be measured directly for polymers by simple heating and evaporation, since polymers degrade before reaching their boiling point.
- The cohesive energy relates to important macroscopic properties like compression modulus, polymer solubility, glass transition temperature, melting temperature...