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Polymer Science 2023

Course Notes of Chapter 3.1

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1. Introduction: Conformations in the Condensed State

This week we turn from isolated chains to polymers in the **condensed state**. In reality, the isolated state is rarely achieved: polymers cannot exist as gases, and the condensed state (liquid, amorphous glassy, semicrystalline, elastomer, thermoset, Slide 113) is the norm. Even dilute solutions are condensed, though chain behavior can resemble that of isolated chains depending on solvent quality. Paradoxically, the most "ideal" conformations occur in the polymer melt where a chain is surrounded by chemically identical neighbors (Slide 108).

2. Macromolecules in the Condensed State

2.1 Forces Between Molecules and Binding Energies

In the condensed state, different types of interactions act within and between macromolecules:

- covalent bonds within chains: ~350–420 kJ/mol (Slides 116, 117).
- secondary (non-covalent) interactions, e.g. dipolar, van der Waals, hydrogen bonding interactions: significantly weaker than covalent bonds; on the order of ~10 kJ/mol per repeat unit.
- repulsion at very short distances (Pauli exclusion)

Because cohesive interactions accumulate with chain length, polymers cannot be vaporized without bond scission. For example, a PE chain with ~100 repeat units already has a cohesive energy > 1000 kJ/mol, exceeding the bond energy of C–C or C–H covalent bonds (Slide 128).

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

The **cohesive energy** is the energy required to separate molecules in a liquid or solid:

$$E_{\mathrm{coh}} = \Delta H_{\mathrm{vap}} - \mathrm{R}T \quad , \tag{1}$$

where ΔH_{vap} is the enthalpy of evaporation and RT accounts for the entropy of the vapor (Slide 127). For polymers, E_{coh} arises from secondary interactions. Attractive contributions often scale as r^{-6}, while repulsion can be approximated as r^{-12}, giving he **Lennard-Jones potential** (per mol):

$$U = -\mathrm{A}r^{-6} + \mathrm{B}r^{-12} \quad , \tag{2}$$

where A and B are constants (Slide 126). Molecules hence adopt an equilibrium separation r_0 that minimizes U. The importance of E_{coh} is evident from its relation to bulk properties such as compression modulus K:

$$K \equiv -V_o \left.\frac{d^2U}{dV^2}\right|_{V=V_o} = \frac{8E_{coh}}{V_o} \quad , \tag{3}$$

with $V_o \cong r^3$ as the molar volume of a polymer segment. The segment is defined somewhat arbitrary, but it makes little sense to assign E_{coh} to an entire chain, since its value would depend on the chain length. Thus, **although E_{coh} cannot be measured directly for polymers, it can be inferred from measurable macroscopic quantities.**

2.3 Relationship Between E_{coh} and Solubility

Polymers cannot be evaporated without degradation, but they can be dissolved. In this case, not only E_{coh} but also solvent–polymer interactions must be considered. The enthalpy of mixing can be written as:

$$\Delta H_{\mathrm{mix}} = E_{\mathrm{coh}}^{1} + E_{\mathrm{coh}}^{2} - 2E_{\mathrm{coh}}^{12} \quad , \tag{4}$$

where E_{coh}^{1} and E_{coh}^{2} are the cohesive energies of the pure components, and E_{coh}^{12} reflects their mutual interaction. Assuming the cross-term can be approximated as the geometric mean leads to the definition of the Hildebrand solubility parameter (Slide 130):

$$\delta = \sqrt{E_{coh}/V_o} \quad , \tag{5}$$

so that

$$\Delta H_{mix} \approx V_o(\delta_1 - \delta_2)^2 \tag{6}$$

In practice, δ for solvents can be obtained directly from evaporation data, while δ for polymers must be estimated indirectly. For better accuracy, δ is decomposed into three contributions:

$$\delta^2 = \delta_{\mathrm{vdW}}^2 + \delta_{\mathrm{d}}^2 + \delta_{\mathrm{h}}^2 \tag{7}$$

representing van-der-Waals, dipolar interactions, and hydrogen-bonding interactions. Solubility can then be mapped experimentally by plotting solvents in the δ-space. The polymer's solubility parameter is taken as the center of a sphere enclosing the "good" solvents (Slide 132).

This framework implies that ΔH_{mix} is always positive and in practice, enthalpic penalties indeed often oppose dissolution, which is therefore largely driven by entropy. Identical solubility parameters minimize this penalty (Equation 6), providing a rational for solubility and enabling a practical classification of good and poor solvents using empirical δ-difference cutoffs. Note, however, that the Gibbs free energy of solvation can still be negative if strong specific interactions (e.g. hydrogen bonding) exist between polymer and solvent.

In Chapter 5, we will extend this picture to polymer-polymer mixtures via Flory-Huggins theory. **Polymer solubility is not only crucial for processing and applications, but also provides a systematic route to estimate E_{coh}, and thus macroscopic properties such as K.** Despite its approximations, this approach has proven remarkably effective (see Slide 133).