Polymer Science 2025/26

Course Notes of Chapter 3.2

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1. Amorphous Polymers and the Glass Transition

1.1 Conformations of an Amorphous Condensed Polymer

An **amorphous polymer** (melt or glass) shows **no long-range order**. Its diffraction pattern (Slide 138) lacks sharp Bragg peaks. Instead, two broad diffuse halos may be identified:

- one from inter-chain spacing (average spacing between chain segments),
- one from intra-chain spacing (average spacing of atoms along the backbone).

Local correlations still exist, but only over 1–2 nm, as in many molecular liquids. Slide 139 (a simulation of PS) shows a random placement and orientation of benzene rings, consistent with chains in **random-coil conformations**, identical to the conformations of isolated, ideal chains (cf. Chapter 2 of the class).

1.2 The Glass Transition

In the melt, chains rapidly explore conformations (like in solution). Upon cooling, mobility decreases sharply. **At the glass transition temperature T_g, conformational motion becomes too slow to follow the cooling rate.** Below T_g, the conformations present in the melt are essentially frozen in place. The polymer remains amorphous as long as crystallization is avoided. Orientation induced in the melt (e.g. by flow) is also frozen in the glass.

Any substance can be glassy if crystallization is bypassed (e.g. by quenching). Metallic glasses are obtained in this way, while silicate glasses (e.g. SiO_2, $T_g \approx 2000$ °C) are not capable to crystallize due to their disordered covalent networks. **Many polymers (atactic PS, PMMA, PC) are also transparent glasses** because the absence of order avoids refractive index variations on >10 nm scales that could cause appreciable scattering of light. By contrast, some glassy materials, such as anthracite, absorb visible light due to their chemical structures and are therefore optically opaque.

1.3 Glass Transition Measurement Techniques

T_g is detected by measuring properties sensitive to molecular mobility (Slides 144–149):

- specific volume (thermal expansion, dilatometry)
- heat capacity (calorimetry)
- elastic modulus (mechanical tests)
- dielectric response etc.

In all methods, the measured T_g depends on the timescale: faster heating/cooling leads to a higher apparent T_g. One can imagine an "intrinsic" glass transition temperature at infinitely slow cooling, T_0. But this cannot be reached experimentally, since the material falls **out of equilibrium** once conformational relaxation times exceed the measurement timescale. **Thus, T_g is not a thermodynamic constant but a kinetic property tied to the measurement timescale.**

1.4 Free Volume Theory

The phenomenology above can be rationalized using the free volume concept which links volume, relaxation times, and viscosity (Slides 150, 151). The idea is that not all volume is rigidly filled: there are "holes" that allow segmental jumps. At high temperatures, more free volume is available and the mobility of the system increases. At lower temperature, the holes shrink, reducing the likelihood of translational motion and conformational rearrangements. T_g corresponds to the point where the conformational changes take so long that the corresponding relaxation times exceed the timescale defined by the cooling rate.

Because the observation time depends on the scanning rate, different rates lead to different experimental glass transition temperatures and different amounts of trapped free volume. **The physical state of the material in the glassy state therefore depends on the rate of cooling. Below T_g, the material is always out-of-equilibrium.**

The model explains why T_g increases with faster cooling, and why viscosity rises steeply as temperature decreases (Vogel-Fulcher-Tammann-Hesse law). Details (derivation, equation, limitations) are given separately in the **Reader on Free Volume Theory**.

The free volume model is very useful but oversimplified. It assumes rigid identical units and neglects polymer chain connectivity as well as specific secondary interactions (e.g. hydrogen bonds). In polymers, above T_g, the system is not a low-viscosity liquid but a **rubber**, with shear modulus $G \approx 1$ MPa. This is much lower than the glassy modulus ($G \approx 1$–2 GPa), but still finite (Slide 148).

Other models exist as well, e.g. a thermodynamic model by **Gibbs and DiMarzio**, which links T_0 to a vanishing configurational entropy (Slide 153). Many variants have been proposed, but none is universally accepted or describes the glass transition in its full nature.

2. T_g and Structure

Although T_g depends on measurement speed a "typical" T_g is usually quoted for each polymer (e.g. by DSC at 10 °C/min). T_g strongly correlates with structure:

- **Chain Stiffness** (Slides 155, 162): **The stiffer the polymer chain the higher is its T_g.** Rigid substituents therefore increase T_g. Example: T_g(PS) ≈ 100 °C vs. T_g(PE) ≈ -100 °C (Slide 155). Aromatic main chain polymers can have $T_g > 200$ °C.

- **Crosslinking** (Slide 160): thermosets usually have a $T_g > 200$ °C, as the high crosslinking density severely restricts segmental mobility. In elastomers, the crosslinking density is usually that low, that the above discussed relations (chain stiffness, molar mass dependence, etc.) hold true.

- **Plasticizers** (Slides 156, 162) reduce the T_g by increasing chain mobility:
  - flexible substituents lower the T_g ("internal plasticization").
  - additives (e.g. phthalates in PVC) lower the T_g ("external plasticization").
  - broad molar mass distributions can act as "self-plasticization".
  - some small solvents can act as antiplasticizers via strong intermolecular interactions.

- **Specific Intermolecular Interactions** (Slides 157 and 162)

  Strong intermolecular interactions (dipole-dipole, ionic, hydrogen-bonds) increase T_g. For example, the T_g of PVC is almost that of PS despite its flexible chains, because of pronounced dipolar interchain interactions. As another important example, polyamides (nylons) show high T_g due to H-bond interactions. However, T_g decreases with humidity (water competes for the H-bonds and acts as an antiplasticizer).

- **Molar Mass** (Slide 158)

  T_g increases with number-average molar mass, M_n, according to the law of Fox-Flory law:

$$T_g = T_{g\infty} - \frac{K}{M_n} \quad , \tag{1}$$

where $T_{g\infty}$ is the hypothetical glass transition temperature of a polymer of infinitely high molar mass and K is a constant. The equation can be rationalized by the free volume theory, assuming that the chain ends contribute additionally to the free volume. The dependence of T_g on molar mass becomes negligible for $M_n \gg 10^4 \mathrm{g/mol}$, but is important during early stages of polymerization (e.g. is the fundamental working principle of cyanoacrylate glue, Slide 159).

In the case of branched polymers, each chain has more than two ends, and therefore an additional free volume even greater than that of a straight chain for a given molar mass. This effect would enhance the plasticizing effect of soft substituents described in Section 2.2. However, the bulky effect of branching on mainchain mobility may be dominant, in which case the T_g increases despite the additional free volume.

- **Copolymerization and Mixtures** (Slide 161)

  For **random copolymers** and **miscible blends**, the T_g often follows the empirical Fox law (binary mixture):

$$\frac{1}{T_g} = \frac{w_1}{T_{g1}} + \frac{w_2}{T_{g2}} \quad , \tag{2}$$

  where T_{g1} and T_{g2} refer to the glass transition temperature of the pure components and w is their mass fraction.

  If, by contrast, phase separation occurs, as in case of immiscible polymer blends or in case of block copolymers ("micro-phase separation”) two distinct T_g values are measured. As an example, **thermoplastic elastomers** are composed of hard blocks (high T_g) that act as physical crosslinks to soft blocks (low T_g) that provide elasticity. Because the glassy “crosslinks” can be molten by heating to a temperature above T_g, the materials can enter a homogenous melt state and reprocessed from there, why they are classified as **thermoplastic**.

3. Summary

- In the amorphous state, chains adopt their ideal random walk conformations. These become frozen at $T < T_g$.
- The glassy state is an out-of-equilibrium state whose physical nature strongly depends on thermal history and how it got approached.

- Free volume theory as a conceptual tool linking specific volume, relaxation times, and viscosity.
- Measurements of T_g by, for example, dilatometry, calorimetry, static mechanical tests, dynamic measurements.
- Structure matters: increasing chain stiffness, molar mass, strength of interchain interactions lead to relative increases in T_g. Plasticizers (internal/external) reduce the T_g.
- Mixtures/copolymers: T_g is tunable by composition unless phase separation occurs.