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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 condensed polymer** (molten or glassy) can be recognized by **the lack of well-defined Bragg peaks in its diffraction pattern** (Slide 123). In general, we only see a broad and diffuse peak (a "diffusion halo") which corresponds to the average separation of the segments of the different chains (the inter-chain spacing), and a second broad and diffuse peak which corresponds to the average spacing of atoms along chains (intra-chain spacing). Thus, if one orients the polymer, by a strong flow for example, so that the chains are elongated in the direction of the orientation, the diffuse peak corresponding to the separation of chains will be in equatorial position (perpendicular) with respect to the orientation, while the intra-chain

spacing will be in a meridional position (parallel to the direction of orientation). The absence of Bragg peaks does not exclude the possibility of local correlations between the chains, which are also present in many liquids made up of small organic molecules, but their range would not exceed 1 to 2 nm.

Slide 124 shows a numerical simulation of polystyrene (PS) in the amorphous state (we recognize the benzene groups that are completely randomly oriented and placed) which reinforces this idea of a very disordered state, in which the individual chains adopt random conformations just like the isolated chains of Chapter 2. In fact, in **an unoriented molten polymer**, **the polymer chains behave like an ideal chain** (Slide 88), that is

$$\langle R_n^2 \rangle = C_\infty n l^2 \qquad (1).$$

1.2 The Glass Transition

In the molten state, which is by definition amorphous, the chains change their conformation very quickly as in solution. However, when the temperature is reduced, **the conformational changes slow down sharply towards the glass transition temperature, T_g, and stop entirely at temperatures below T_g. The conformations in the glassy state are therefore a snapshot of the conformations in the molten state**. The polymer remains amorphous as long as it does not crystallize above T_g, and our expression for R_n remains valid if the average is taken over a large number of chains and in the absence of orientation (note that any orientation induced by molten flow would also be frozen in the glassy state).

In principle any substance can exist in an amorphous state if it can be avoided that it crystallizes before falling below its T_g, for example by very fast cooling so that it does not have time to crystallize. This is how metallic glasses are obtained, but in the case of inorganic glasses such as silicate glasses, the glass transition, which is around 2000 °C for pure SiO_2, is linked to the formation of a disordered network of covalent bonds which cannot crystallize. It is noted that silicate glasses, just like **PS (atactic), PMMA (atactic) and glassy PC, are transparent.** There is no ordered structure and therefore no large variations in the refractive index at the scale of >10 nm that could cause appreciable scattering of light. However, some glasses (carbon, for example) absorb visible light due to their chemical structures and are therefore colored or even opaque.

1.3 Glass Transition Measurement Techniques

It follows that **techniques for measuring T_g are based on properties that reflect changes in mobility**, such as the thermal expansion coefficient, heat capacity, modulus of elasticity, or dielectric constant. Some of these techniques are illustrated in Slides 127-134. We notice in all cases, that **the measured T_g increases with the measurement speed** (Slides 126-128, 131, 132), whether the measurement is made by heating or by cooling. We can suppose that there is an "intrinsic" value of T_g in the limit where the speed of measurement tends towards 0 (let us

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call it T_o) and where the materials turns glassy under equilibrium conditions. But, since one cannot make infinitely slow measurements, one can never reach the state of the material corresponding to this temperature. **The material is therefore out of equilibrium at temperatures below the measured T_g.** The glass transition is therefore not a thermodynamic transition.

We will try to illustrate this idea by considering the example of the thermal expansion coefficient (Slide 126).

- At temperatures well above T_g the system is in equilibrium, the molecules being able to change their conformation very quickly so as to minimize the overall potential energy of the system, which will be characterized by a well-defined value of the specific volume at a given temperature T, $V(T)$, which in turn will depend on the anharmonicity of the intermolecular potential and the thermal energy of the molecules.
- If we reduce T and therefore the thermal energy, as long as the molecules can change their conformation freely, V(T) will decrease. The coefficient of thermal expansion in the liquid state is thus defined:

$$\alpha_{liquid} = \frac{1}{v_o}\frac{dV(T)}{dT}\bigg|_{liquid} \qquad (2),$$

  where v_o is the volume that the system would occupy at equilibrium in the absence of thermal energy. α_{liquid} is approximately constant.
- Now, we admit that when we decrease the volume of the system, it is increasingly difficult for molecules to move. In other words, the so-called **"relaxation" time, τ,** which they need to change their conformation, becomes longer. Now, if we reduce the temperature at a constant rate, $\Theta = \mathrm{d}T/\mathrm{d}t$, the time, Δt that the molecules take to go from a temperature T_1 to a temperature T_2 will be equal to

$$\Delta t = \frac{T_1 - T_2}{\Theta} \qquad (3).$$

- If the average value of τ in this interval of T is longer than Δt, the molecules will not be able to change their conformation and the conformations will remain locked if we continue to cool. The system can no longer come close to equilibrium.
- $V(T)$ will still continue to decrease as we reduce T and therefore the thermal vibrations of molecules, but with a reduced thermal expansion coefficient, because the molecules can no longer change their conformation and undergo translational motion,

$$\alpha_{glass} = \frac{1}{v_o}\frac{dV(T)}{dT}\bigg|_{glass} \qquad (4).$$

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- As shown in Slide 126, the temperature where $V(T)$ changes sharply in slope provides an experimental measure of T_g, which will be higher for higher cooling rates. We speak of a second order transition, because the change of V remains continuous, and it is its derivative that changes in a discontinuous manner (in contrast to a crystallization process, where the change in V is abrupt).

1.4 The Theory of Free Volume

We will now try to formalize these ideas a little more by considering a simplified system composed of rigid and identical balls (Slide 135). In the absence of thermal vibrations (at $T = 0$ K, therefore) after an infinitely slow cooling, each of these balls would occupy a volume v_o which would include the volume of the ball as well as a certain unoccupied volume (the interstices).

Let's start at a temperature well above T_g where the average volume per ball is $V(T)$, which we will express as follows, using Equations 2 and 4 and with the temperatures in K

$$V(T) = \left.\frac{dV(T)}{dT}\right|_{glass} T + v_{fm}[T - T_o] = \alpha_{glass} v_o T + (\alpha_{liquid} - \alpha_{glass}) v_o (T - T_o) \quad (5),$$
$$= \alpha_{glass} v_o T + \Delta\alpha v_o (T - T_o)$$

where v_{fm} is the average free volume per ball, i.e. the excess volume in the liquid state compared to the volume per ball that our "material" would have at this temperature if the balls occupied the same positions as at $T = 0$ K after infinitely slow cooling, and T_o is a characteristic temperature of the material (Slide 135).

So, what does T_o mean? It is assumed **that T_o is a temperature where part of the volume created by thermal vibrations is "free" to redistribute within the material, thus creating holes. If one of these holes gets close to the size of a ball, there may be enough room for a ball to change position**. As thermal energy increases, the arrangement of the entire system can begin to change to minimize its energy. However, no movement is possible below T_o. The system is frozen.

We suppose now that the relaxation time, τ, associated with the ball movements is given by

$$\tau = \tau_o \exp\left[v_o / v_{fm}\right] = \tau_o \exp[\Delta\alpha^{-1}/(T - T_o)] \quad (6),$$

where τ_o is a constant. This implies the viscosity of the system, which is proportional to τ, to be

$$\eta = \eta_o \exp[\Delta\alpha^{-1}/(T - T_o)] \quad (7),$$

which reflects the behavior observed in many glass forming systems. Indeed, Equation 7 is formally identical to the empirical equation of Volger, Fulcher, Tamman and Hesse (VFT or VFTH) which dates from the 1920s.

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Let's go back to our system well above T_g which has volume $V(T)$, which is a unique function of T (Equation 5), because the system is at equilibrium. For a finite cooling rate Θ, the motions of the balls will be effectively suppressed at a critical value of τ and therefore at a temperature $T > T_0$ which will be the experimental T_g. **The experimental T_g will increase with Θ.** Moreover, as shown in Slide 136, a quantity of free volume per bead equal to $\Delta\alpha v_o(T_g - T_o)$ will therefore be trapped in the glassy state (it is estimated that the trapped free volume in an amorphous polymer in the glassy state is of the order of 2.5% of the total volume). **The physical state of the material in the glassy state hence depends on the rate of cooling**.

If the material is now heated at the same speed Θ, the balls will again have enough time to move when the temperature reaches the value of T_g measured previously upon cooling. On the other hand, if you heat at a rate higher than the initial cooling rate, it will require more volume and therefore a higher temperature for the balls to start moving, which is reflected by higher measured T_g. What happens if you heat at a slower rate than the initial cooling rate (see the corresponding Exercise Sheet 6)?

1.5 Limitations of This Approach

The free volume model describes well certain aspects of the phenomenology of the glass transition, in particular, **as it is a kinetic model, the variation of the T_g measured as a function of the measurement speed** (the heating or cooling speed) and **the variation of viscosity as a function of temperature** (Equation 7), **as well as other properties of interest to the engineer**, as we will see later. However, it is based on a very simple liquid, and does not take into account, for example, the connectivity of a macromolecular chain, for which each bead in the model would represent only one segment, nor secondary interactions. We will learn soon that, unlike a glass composed of small molecules, **a polymer of high molar mass does not turn into a liquid above T_g, but into a "rubber", with a shear modulus on the order of 1 MPa, i.e. some 3 orders of magnitude lower than the glassy shear modulus (typically 1–2 GPa for an amorphous polymer)** (Slide 132).

Moreover, the free volume model does not at all address the true physical nature of the transition that is supposed to take place at T_o and of which T_g is only a manifestation. Nevertheless, as we will see in Section 2, it is observed that any change in the chemical structure of a polymer that leads to a reduced mobility has a tendency to increase T_g, such as, for example, an increased chain rigidity or the presence of strong specific intermolecular interactions. This is logical, given that the glass transition involves a loss of mobility - if the mobility is already low one can imagine that this transition takes place at a rather high temperature.

1.6 Other Models

There are many other models for the glass transition, one of the best known being that of **Gibbs and DiMarzio**. This is a **thermodynamic model for T_o based on the theory of Flory-Huggins mixtures** (see Chapter 5 of the class), including holes and chains, using activation energies for

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hole formation and chain conformational changes. They thus showed that the entropy of a liquid should reach a state of configurational entropy (these are the "configurations" of the system, though the word does not have the same meaning here as when talking about the chemical configuration of a chain) of zero. However, this model does not shed much light on the fundamental nature of the phenomenon. Indeed, an expert (David A. Weitz, Harvard University) said in 2008, “There are more theories [and simulations] of the glass transition than there are theorists who propose them,” but it remains difficult to discriminate between these different theories based on observations.

2. T_g and Structure

Though T_g varies with the measurement speed, in general a “typical” value is admitted for each polymer which approximately corresponds to a calorimetric measurement with a heating rate of 10 K/min. Slide 140 and the following list the T_g of some examples and also show interesting correlations between chemical structure and T_g.

2.1 Chain Stiffness and Crosslinking (Slides 140, 147)

By **increasing the size of a rigid substituent in a vinyl chain, which has the effect of increasing the rigidity of the chain** (*cf.* to Chapter 2 of our class), **the T_g is increased**. Thus, PS has a T_g of 100 °C, i.e. nearly 200 °C higher than that of PE (first series of Slide 147). In certain “technical” thermoplastics whose main chains contain aromatic catenary units, as well as highly crosslinked thermosets (Slide 145), the T_g can exceed 200 °C.

2.2 Plasticizers (Slides 141 and 147)

If the substituent is a flexible chain, this trend can be reversed. Thus, by switching from PP (CH_3) to polybutene (CH_2-CH_3) and so on (Slide 147) we observe a decrease in T_g (and for a sufficiently long substituent of (CH_n-CH_3) type we approach the T_g of PE). We speak of **internal plasticization** because the unit which decreases the T_g (the plasticizer) is chemically bound to the polymer. You find another example in Slide 141.

The T_g can also be reduced simply by mixing the polymer with a suitable additive, in which case we speak of **external plasticization**. External plasticization is **mainly used for PVC**, which forms a stable mixture with certain polar oils such as butyl or diethylhexyl phthalate in proportions of up to 15 to 30%, making it progressively more flexible. We also speak of "**self-plasticization**" in the case of certain polyolefins (PE, PP) thanks to their wide molar mass distribution so that the small chains plasticize the large ones.

Finally, the presence of small amounts of a good solvent can have an **antiplasticizing** effect due to the strong polymer-solvent interactions.

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2.3 Specific Intermolecular Interactions (Slides 142 and 147)

We also notice that the presence of polar or ionic groups which reinforce the secondary interactions between the chains (to make them more "sticky") increases the T_g. Thus, PVC has a T_g almost as high as that of the PS (fourth series of Slide 147). Another very important example is that of polyamides (Nylons, PA) illustrated on Slide 142, where the hydrogen bonds formed by the amide groups cause a significant increase in T_g compared to PE despite the flexibility of the chains of an aliphatic polyamide like PA66. In this case, the amide groups can also form hydrogen bonds with water. The T_g of polyamides is therefore very sensitive to humidity, which acts as a plasticizer, because it breaks the hydrogen bonds that directly connect the molecules of the polymer.

2.4 Molar Mass (Slide 143)

There is an increase in T_g with the number average molar mass, M_n, according to the law of FLory-Fox

$$T_g = T_{g\infty} - \frac{K}{M_n} \qquad (8).$$

The free volume model provides an explanation for this. It is assumed that each end of the chain provides additional free volume, θ. At a given measurement speed, the glass transition which corresponds to an infinite M_n, which we will call $T_{g\infty}$, will take place at a critical value of the free volume per segment (Equation 5)

$$v_{fmc} = (\alpha_{liquid} - \alpha_{glass}) v_o (T_{g\infty} - T_o) \qquad (9).$$

Since there are $2\rho N_A/M_n$ chain ends per unit volume, where ρ is the density and N_A is the Avogadro number,

$$v_{fm}(M_n, T_{g\infty}) = v_{fmc} + v_o \frac{2\theta\rho N_A}{M_n} \qquad (10).$$
$$= (\alpha_{liquid} - \alpha_{glass}) v_o (T_{g\infty} - T_o) + v_o \frac{2\theta\rho N_A}{M_n}$$

Assuming that the glass transition always takes place when $v_{fm}(M_n) = v_{fmc}$,

$$(\alpha_{liquid} - \alpha_{glass}) v_o (T_{g\infty} - T_o) = (\alpha_{liquid} - \alpha_{glass}) v_o (T_g - T_o) + v_o \frac{2\theta\rho N_A}{M_n} \qquad (11).$$

$$T_g = T_{g\infty} - \frac{2\theta\rho N_A}{(\alpha_{liquid} - \alpha_{glass}) M_n}$$

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which has the same form as Equation 8. Note that for the molar masses of commercial polymers of several tens of thousands of g/mol, the second term becomes negligible and $T_g \cong T_{g,\infty}$. On the other hand, in certain situations such as the onset of polymerization, T_g can vary significantly. An example of practical importance is the anionic polymerization of a cyanoacrylate glue (Slide 144). The monomer is a low viscosity liquid which begins to polymerize on contact with ambient humidity. When M_n is high enough, T_g exceeds room temperature and the glue "sets" - it becomes glassy and strong.

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 branchings on mainchain mobility may be dominant, in which case the T_g increases despite the additional free volume.

2.5 Copolymerization and Mixtures

For a homogeneous and amorphous mixture of different polymers (in fact, most polymers are immiscible as seen in Chapter 4.2) or a random copolymer of two or more different monomers, the **T_g generally follows a simple mixing law** such as, for example, Fox's law for a binary mixture

$$\frac{1}{T_g} = \frac{w_1}{T_{g1}} + \frac{(1-w_1)}{T_{g2}} \qquad (12).$$

where 1 and 2 refer to the T_g of the pure components and w is the mass fraction. These are only empirical laws and there are many other possibilities. Nevertheless, it is assumed that the T_g of a homogeneous and amorphous mixture or copolymer can be changed systematically by varying the composition, which is a method widely used in practice to control the T_g of some systems.

Obviously, **if there is phase separation** (or "micro-phase separation" in the case of a block copolymer), **two different T_g are measured**. This can also be of practical use. For example, some polyurethanes are "segmented" or "multi-block" linear polymers. While the longer blocks are generally soft with a very low T_g, the "hard" blocks with a very high T_g act as physical crosslink points. In this case, the glassy "crosslinks" can be molten by heating to a temperature above the T_g of the hard blocks. We therefore classify these materials as **thermoplastic elastomers**.

3. Summary

- In the amorphous state, chains adopt their ideal random walk conformations. These become frozen at $T < T_g$.

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- We can measure T_g by, for example, dilatometry, calorimetry, static mechanical tests, dynamic measurements.
- A high T_g is favored by high M, high chain stiffness, strong interchain forces (specific interactions).
- If necessary one can reduce the T_g using plasticizers.

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