Morphology of polymers: The crystalline and the amorphous state (contd.)

Factors affecting crystallinity and $T_m$:

The following factors are to be considered:

A] Symmetry: The symmetry of the chain shape influences both $T_m$ and the ability to form crystallites. Polyethylene and poly(tetrafluoroethylene) are both sufficiently symmetrical to be considered smooth stiff cylindrical rods. In the crystal, these rods tend to roll over each other and change position when thermally agitated. This motion within the crystal lattice, called *premelting*, increases the entropy of the crystal and effectively stabilizes it. Consequently, more thermal energy is required before the crystal becomes unstable, and $T_m$ is increased. Flat or irregularly shaped polymers, with bends and bumps in the chain, cannot move in this way without disrupting the crystal lattice, and so have lower $T_m$ values. This is only one aspect.

For crystallite formation in a polymer, easy close-packing of the chains in a regular three-dimensional fashion is required. Again, linear symmetrical molecules are best. Polyethylene, poly(tetrafluoroethylene), and other chains with more complex backbones containing –(O)–, –(COO)–, –(CONH)– and groups all possess a suitable symmetry for crystallite formation, and usually assume extended zigzag conformations when aligned in the lattice.

Chains containing irregular units, which detract from the linear geometry, reduce the ability of a polymer to crystallize. Thus, cis-double bonds (A), o- and m-phenylene groups (B), or cis-oriented puckered rings (C) all encourage bending and twisting in the chains and make regular close-packing very difficult. If, however, the phenylene rings are *para*-oriented, the chains retain their axial symmetry and can crystallize more readily. Similarly, incorporation of a trans-double bond maintains the chain symmetry. This is highlighted when comparing the amorphous elastomeric cis-polyisoprene ($T_m$ 301 K) with the highly crystalline trans-polyisoprene ($T_m$ 347 K), which has no virtue as an elastomer, or cis-poly(1,3-butadiene) ($T_m$ = 262 K) with trans-poly(1,3-butadiene) ($T_m$ = 421 K).

B] Intermolecular non-covalent interactions: In polyethylene crystallites, the close packing achieved by the chains allows the van der Waals forces to act cooperatively and provide additional stability to the crystallite. Any interaction between chains in the crystal lattice will help to hold the structure together more firmly and raise the melting temperature. Polymers containing polar groups, e.g., Cl, CN, or OII, can be held rigid, and aligned, in a polymer matrix by the strong dipole–dipole interactions between the substituents, but the effect is most obvious in the symmetrical polyamides. These polymers can form intermolecular hydrogen bonds, which greatly enhance crystallite stability. This is illustrated in the following figure for nylon-6,6, where the extended zigzag conformation is ideally suited to allow regular intermolecular hydrogen bonding. The increased stability is reflected in $T_m$, which for nylon-6,6 is 540 K compared to 410 K for polyethylene.
Extended zigzag structures for (a) nylon-6,6 and (b) nylon-7,7 showing the allowed hydrogen bonding.

The structures of related polyamides do not always lead to this neat arrangement of intermolecular bond formation. For example, the geometry of an extended nylon-7,7 chain allows the formation of only every second possible hydrogen bond when the chains are aligned and fully extended. However, the process is so favourable energetically that sufficient deformation of the chain takes place to enable formation of all possible hydrogen bonds. The added stability that these bonds impart to the crystallite far outweighs the limited loss of energy caused by chain flexing.

Secondary bonds can therefore lead to a stimulation of the crystallization process in the appropriate polymers.

Strong intermolecular forces and a stiff chain backbone favour the formation of crystals because the molecules prefer an ordered arrangement with maximum packing density to maximize the number of secondary bonds. As we have seen, these molecules tend to cooperatively organize and develop a crystalline structure. Another good example is Kevlar, an aromatic polyamide (aramid) which has a high degree of crystallinity. The polar amide groups in the backbone are strongly attracted to each other and form strong hydrogen bonds. This raises the glass transition temperature (580-620 K) and the melting point (833 K for Kevlar 49). The high crystallinity and strong intermolecular interactions also greatly increases the mechanical strength. In fact, Kevlar fibres are some of the strongest plastic fibres on the market.
H-bonding in Kevlar-49

C) Tacticity: Chain symmetry and flexibility both affect the crystallinity of a polymer sample. If a chain possesses large pendant groups, these will not only increase the rigidity but also increase the difficulty of close packing and, hence, the formation of a crystalline array. This latter problem can be overcome if the groups are arranged in a regular fashion along the chain. Isotactic polymers tend to form helices to accommodate the substituents in the most stable steric positions; these helices are regular forms capable of regular alignment. Thus, atactic polystyrene is amorphous, but isotactic polystyrene is semicrystalline (T_m = 513 K).

Syndiotactic polymers are also sufficiently regular to crystallize, not necessarily as a helix but rather as glide planes.

Branching in the side group tends to stiffen the chain and raise T_m, as shown in the series pol(y-but-1-ene), T_m = 399 K; pol(y-3-methyl but-1-ene), T_m = 418 K; and pol(y-3,3'-dimethyl but-1-ene), T_m > 593 K.

If the side group is flexible and nonpolar, T_m is lowered. For such a flexible polymer chain there is a large change in entropy on going from the crystalline phase to the melt. On the other hand, if the polymer chain is stiff, because of the presence of bulky groups in the backbone, for example, then the change in entropy associated with melting will be less than for a more flexible polymer and this will tend to make the melting temperature higher for the former.

In general, oxygen groups in the backbone of the polymer (ether and ester functional groups) tend to make it more flexible, while benzene rings make it "stiffer". This can be illustrated by examining the melting temperatures of the following three polymers, where the intermolecular forces are roughly the same (dispersion, weak polar):
The presence of bulky groups attached to the side chain can also raise the melting temperature, as bond rotations are inhibited by steric hindrance and the number of configurations available to the chain becomes limited:

\[
\begin{align*}
T_m \text{ (°C)} & \\
\text{poly(ethylene oxide)} & 65 \\
\text{polythene} & 135 \\
\text{poly(p-xylene)} & 400
\end{align*}
\]

D) Branching and molar mass: If the chain is substantially branched, the packing efficiency deteriorates and the crystalline content is lowered. Polyethylene provides a good example (vide the adjacent figure), where extensive branching lowers the density and \( T_m \) of the polymer.

Specific volume \( \nu \) plotted against temperature \( T \) for a sample of linear polyethylene annealed for 40 d and a branched sample. Points A and B are the respective melting temperatures.
Molar mass can also alter $T_m$. The end units on a chain are chemically different. They are usually bulkier than the repeating segments and therefore excluded from the lattice. Obviously, as the chain length (molecular weight) of the polymer is increased the number of end-groups is proportionally decreased and the melting temperature increases. This is not a linear increase, however, and the melting point approaches an asymptotic limit at high molecular weights.

Another way of looking at it is to consider the relative freedom of chain ends to move and if the number of such chain ends is increased by reducing the molar mass, then $T_m$ is lowered because of the decrease in energy required to stimulate chain motion and melting. For example, polypropylene, with $M = 2000 \text{ g mol}^{-1}$, has $T_m = 387 \text{ K}$, whereas a sample with $M = 30,000 \text{ g mol}^{-1}$ has $T_m = 443 \text{ K}.$

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