Structure–Property Relationships of Small Organic Molecules as a Prelude to the Teaching of Polymer Science

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ABSTRACT: Small organic molecules offer a rich opportunity to discuss the interplay of chemical structure with properties such as the melting point and phenomena such as glass formation and can form the basis of fundamental considerations of structure–property relationships in macromolecules. Of particular importance are thermal transitions, specifically melting points and glass transition temperatures, and each is discussed in the context of structure–property correlations. Connections are made to a few commercially important polymers and their thermal transitions.

KEYWORDS: Polymer Chemistry, Organic Chemistry, Physical Chemistry, Materials Science, Thermodynamics

INTRODUCTION

The term “structure–property relationship” and its implications pervade all of polymer science and engineering. For example, subtle changes in the repeating unit of a polyamide can alter the melting point, the degree of moisture uptake, and the mechanical properties, which in turn can dictate the scope and limitations of a commercial application. While certain properties such as the very high mechanical strength of selected polymer fibers are a characteristic only of long-chain molecules, many other properties have a dependence on molecular structure that can parallel that of small molecule analogues, and therefore, it is sensible to discuss the latter first.

In general, the physical properties of organic molecules are determined by four factors: (1) molecular weight and therefore molecular size, (2) symmetry, (3) conformational flexibility, and (4) the nature and strength of intermolecular forces. We will discuss briefly here how these factors influence melting points and the ability to form amorphous (noncrystalline) solids known as glasses. We begin our discussion with melting point trends for linear or normal alkanes.

MELTING POINTS OF ALIPHATIC HYDROCARBONS

The second law of thermodynamics tells us that at the melting point, solid and liquid phases coexist in equilibrium. Thus, ΔG_m = 0, and the melting temperature T_m is simply equal to ΔH_m/ΔS_m, the ratio of the enthalpy and entropy of melting (or fusion). The normal alkanes are prototypical nonpolar molecules, in which intermolecular or secondary forces are the result of instantaneous dipoles due to transient, non-symmetric electron distributions within bonds that induce transient dipoles on neighboring molecules. These relatively weak (1–10 kJ/mol) interactions are called London dispersion, or van der Waals forces. Since larger molecules present a larger “surface area” over which dispersion forces may operate, the magnitude of these forces is expected to increase with molecular weight, and accordingly, the melting point is expected to increase as a result of the increase in ΔH_m with increasing molecular weight.

The argument is not complete, however, without some mention of the entropy contribution. It should be noted that n-alkanes exist in the all-trans conformation or the so-called “zigzag” structure, in which the conformation of each C–C bond is anti in the solid state; this highly regular structure facilitates close molecular packing and thus maximizes intermolecular forces. Upon melting, n-alkane molecules may adopt a variety of conformations besides the all-trans form, as the barriers to interconversion of rotational isomers, or conformers, are relatively small. A few conformers of n-pentane wherein the C–C bonds lie in a plane are shown in Figure 1, and there are of course many more in three dimensions. The great number of alternative conformations that are accessible in the liquid state would suggest that a rather large entropy increase should accompany melting. Moreover, the number of alternative conformations for n-alkanes should increase dramatically with molecular weight.

Let us now consider the dependence of the melting point of a linear aliphatic hydrocarbon on the number of carbon atoms, taking into account the relative importance of ΔH_m and ΔS_m in determining T_m. Data for selected molecular weights can be found in Table 1. Three observations deserve attention: (i) the melting point does increase with molecular weight as would be expected, although (ii) the dependence on molecular weight becomes less pronounced as the molecular weight increases (Figure 2) and (iii) for n-alkanes with less than about 18 carbons, the overall trend is not smooth (Figure 3). The increase in T_m with number of carbons and hence molecular weight is the result of increasing ΔH_m, but the concomitant large increase in ΔS_m due to the high flexibility of a linear hydrocarbon chain tempers the T_m rise. Interestingly, at high molecular weights T_m levels off at about 140 °C, which is the melting temperature of linear or high-density polyethylene. An explanation based on the segment picture of polymer chains was offered by Eyring and co-workers many years ago. The T_m per methylene group can be determined from the slope of a line drawn through the data points of Figure 2 up to about 20...
carbons and is found to be about 20 K per methylene. Extrapolation of that line to 413 K (140 °C), the $T_m$ of linear, high-molecular-weight polyethylene, gives an estimated segment length of roughly 413/20 or about 21 methylene units. In essence, beyond a critical number of carbons in the backbone, which defines a segment, it is the $\Delta H_m$ and $\Delta S_m$ of the segments, which act essentially independently of one another at high molecular weights, that define and limit $T_m$. Incidentally, the limiting behavior of $T_m$ as a function of molecular weight is not exclusive to polyethylene since the segment picture has broad applicability.

The alternation behavior seen in Figure 3 for $T_m$ of the n-alkane series up to 18 carbons is the result of differences in packing of the end groups (methyls in these cases) in the crystals,$^3$ and this behavior decays with increasing number of carbons as the end-group effects become diluted.

In cases where isomerism for an alkane is possible, i.e., beyond propane, the melting point can be higher or lower relative to that of the $n$-alkane depending on the symmetry and

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Table 1. $T_m$, $\Delta H_m$, and $\Delta S_m$ as Functions of the Number of Carbons and Molecular Weight for Selected $n$-Alkanes

<table>
<thead>
<tr>
<th>Compound</th>
<th>Number of Carbons</th>
<th>$T_m$ °C</th>
<th>$T_m$ K</th>
<th>MW, g/mol</th>
<th>$\Delta H_m$, kJ/mol</th>
<th>$\Delta S_m$, J mol$^{-1}$ K$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pentane</td>
<td>5</td>
<td>−129.7</td>
<td>143.3</td>
<td>72</td>
<td>8.42</td>
<td>58.79</td>
</tr>
<tr>
<td>Hexane</td>
<td>6</td>
<td>−94.4</td>
<td>178.6</td>
<td>86</td>
<td>13.07</td>
<td>73.19</td>
</tr>
<tr>
<td>Heptane</td>
<td>7</td>
<td>−90.5</td>
<td>182.5</td>
<td>100</td>
<td>14.10</td>
<td>77.26</td>
</tr>
<tr>
<td>Octane</td>
<td>8</td>
<td>−56.8</td>
<td>216.2</td>
<td>114</td>
<td>20.63</td>
<td>95.44</td>
</tr>
<tr>
<td>Nonane</td>
<td>9</td>
<td>−53.7</td>
<td>219.3</td>
<td>128</td>
<td>21.76</td>
<td>99.22</td>
</tr>
<tr>
<td>Decane</td>
<td>10</td>
<td>−29.7</td>
<td>243.3</td>
<td>142</td>
<td>28.68</td>
<td>117.90</td>
</tr>
<tr>
<td>Undecane</td>
<td>11</td>
<td>−25.6</td>
<td>247.4</td>
<td>156</td>
<td>27.61</td>
<td>111.61</td>
</tr>
<tr>
<td>Dodecane</td>
<td>12</td>
<td>−9.7</td>
<td>263.3</td>
<td>170</td>
<td>36.72</td>
<td>139.46</td>
</tr>
<tr>
<td>Tridecane</td>
<td>13</td>
<td>−6.0</td>
<td>267.0</td>
<td>184</td>
<td>36.06</td>
<td>135.07</td>
</tr>
<tr>
<td>Tetradecane</td>
<td>14</td>
<td>5.5</td>
<td>278.5</td>
<td>198</td>
<td>44.95</td>
<td>161.39</td>
</tr>
<tr>
<td>Pentadecane</td>
<td>15</td>
<td>10.0</td>
<td>283.0</td>
<td>212</td>
<td>43.88</td>
<td>155.07</td>
</tr>
<tr>
<td>Hexadecane</td>
<td>16</td>
<td>18.1</td>
<td>291.1</td>
<td>226</td>
<td>53.34</td>
<td>183.22</td>
</tr>
<tr>
<td>Heptadecane</td>
<td>17</td>
<td>22.0</td>
<td>295.0</td>
<td>240</td>
<td>51.36</td>
<td>174.10</td>
</tr>
<tr>
<td>Octadecane</td>
<td>18</td>
<td>28.0</td>
<td>301.0</td>
<td>254</td>
<td>61.98</td>
<td>205.90</td>
</tr>
<tr>
<td>Nonadecane</td>
<td>19</td>
<td>32.1</td>
<td>305.1</td>
<td>268</td>
<td>59.50</td>
<td>195.00</td>
</tr>
<tr>
<td>Eicosane</td>
<td>20</td>
<td>36.7</td>
<td>309.7</td>
<td>282</td>
<td>69.94</td>
<td>225.61</td>
</tr>
<tr>
<td>Pentacosane</td>
<td>25</td>
<td>53.6</td>
<td>326.6</td>
<td>352</td>
<td>83.78</td>
<td>256.51</td>
</tr>
<tr>
<td>Triacontane</td>
<td>30</td>
<td>65.5</td>
<td>338.5</td>
<td>422</td>
<td>106.34</td>
<td>314.16</td>
</tr>
<tr>
<td>Pentatriacontane</td>
<td>35</td>
<td>74.8</td>
<td>347.8</td>
<td>492</td>
<td>126.64</td>
<td>363.55</td>
</tr>
<tr>
<td>Tetracontane</td>
<td>40</td>
<td>81.6</td>
<td>354.6</td>
<td>562</td>
<td>152.86</td>
<td>431.09</td>
</tr>
<tr>
<td>Pentaccontane</td>
<td>50</td>
<td>92.2</td>
<td>365.2</td>
<td>702</td>
<td>193.75</td>
<td>530.53</td>
</tr>
<tr>
<td>Hexacontane</td>
<td>60</td>
<td>99.2</td>
<td>372.2</td>
<td>842</td>
<td>234.91</td>
<td>631.14</td>
</tr>
<tr>
<td>Heptacontane</td>
<td>70</td>
<td>105.7</td>
<td>378.7</td>
<td>982</td>
<td>275.94</td>
<td>728.65</td>
</tr>
<tr>
<td>Hectane</td>
<td>100</td>
<td>115.4</td>
<td>388.4</td>
<td>1402</td>
<td>399.57</td>
<td>1028.76</td>
</tr>
</tbody>
</table>

Data from ref 1.

Figure 1. All-trans conformers of $n$-pentane in the solid state compared with a few conformers in the melt.
conformational flexibility of the molecule. For example, consider the data in Table 2 for the three isomers of C5H12, namely, n-pentane, 2-methylbutane, and 2,2-dimethylpropane, the latter also known as neopentane. The lowest \( T_m \) is exhibited by 2-methylbutane, which has a lower \( \Delta H_m \) than n-pentane, presumably because of poorer packing in the crystalline state, and a lower but still significant \( \Delta S_m \) with fewer conformations available in the melt. However, 2,2-dimethylpropane melts at the comparatively high temperature of -17 °C. Even though this is a highly symmetric molecule, the high \( T_m \) cannot be the result of stronger intermolecular forces per the low \( \Delta H_m \) but is rather the result of a much lower \( \Delta S_m \): the compact, essentially

![Figure 2](image_url1)

**Figure 2.** Plot of \( T_m \) vs number of carbons for the \( n \)-alkane series in Table 1.

![Figure 3](image_url2)

**Figure 3.** Plot of \( T_m \) vs number of carbons for the \( n \)-alkane series up to C18.
spherical molecule is not capable of assuming numerous conformations because of rotational isomerism and has principally only translational entropy in the liquid state.

LESSONS FROM TWO ADDITIONAL MOLECULES: MELTING POINTS OF ANTHRACENE AND BENZOIC ACID

Table 2 also presents relevant data for two other simple organic compounds, anthracene and benzoic acid. Anthracene is a 14-carbon molecule, and it is interesting to compare its properties with those of the C-14 alkane tetradecane in Table 1. It should be noted that although $\Delta H_m$ for anthracene is smaller than that for tetradecane, $\Delta S_m$ for anthracene is even smaller in relative terms, reflecting a lack of conformational flexibility; hence, anthracene’s $T_m$ is quite high.

The melting point of benzoic acid is relatively high, and it is tempting to suggest that this is because it is necessary to overcome the rather strong hydrogen bonds between carboxylic acid groups. However, the $\Delta H_m$ is less than that of the nonpolar molecule $n$-octane. This is because the hydrogen bonds are at least partially re-established in the melt in the form of hydrogen-bonded dimers. As a result, the entropy of the melt is considerably less than it would be in the absence of dimer formation. Thus, we conclude that the high melting point of benzoic acid is principally the result of a relatively low entropy of melting.

GLASSES

Imagine cooling a liquid of a relatively low molecular weight organic compound such as methylcyclohexane. You might expect to see solidification in the form of crystallization once the freezing point is reached. If you carefully measured volume changes, you would see a rather sharp decrease in volume at the freezing point. However, upon cooling from the liquid (melt), it is possible to bypass $T_m$ and obtain a noncrystalline, e.g., glassy, solid if molecular motion effectively ceases before the molecules are able to arrange themselves appropriately for crystallization to occur. Generically, a glass can be defined as a substance with the physical properties of a solid but the structural properties of a liquid. In other words, a glass is an

<table>
<thead>
<tr>
<th>Compound</th>
<th>$T_m$ K</th>
<th>$\Delta H_m$ kJ/mol</th>
<th>$\Delta S_m$ J/mol-K</th>
</tr>
</thead>
<tbody>
<tr>
<td>pentane</td>
<td>143</td>
<td>8.42</td>
<td>58.80</td>
</tr>
<tr>
<td>2-methylbutane</td>
<td>113</td>
<td>5.10</td>
<td>43.10</td>
</tr>
<tr>
<td>2,2-dimethylpropane</td>
<td>256</td>
<td>3.22</td>
<td>12.97</td>
</tr>
<tr>
<td>anthracene</td>
<td>490</td>
<td>28.80</td>
<td>58.77</td>
</tr>
<tr>
<td>benzoic acid</td>
<td>395</td>
<td>17.31</td>
<td>43.82</td>
</tr>
</tbody>
</table>

“Data from ref 4.
amorphous solid. The process of glass formation is called vitrification. While we readily identify the term "glass" with inorganic network substances such as silica glass, many organic polymers, organic small molecules, and even metals can and do exist as glasses. In fact, methylcyclohexane is an example of a small organic molecule that is able to form a glass.

Glass formation can be encouraged in the following ways: (1) very rapid cooling; (2) a lack of molecular symmetry, which can inhibit close packing and crystallization; (3) the presence of large rotational barriers that may retard the attainment of a conformation necessary for crystallization; and (4) attainment of a high viscosity near the melting temperature, which can inhibit proper packing. In the case of methylcyclohexane, the molecule is asymmetric, having equatorial and axial conformers, and rapid cooling (e.g., a plunge into liquid N₂) can lead to the formation of a glass.

The temperature at which vitrification occurs is called the glass transition temperature and is designated as \( T_g \). Figure 4 compares the formation of a glass with crystallization, where in the former the normal crystallization process with a well-defined \( T_m \) is bypassed, leading to a supercooled liquid. Eventually, molecular motions effectively cease, and a glass is formed. It should be noted that the specific volume of a glass is higher than that of a crystalline form of the same material since molecules in the glass cannot reorganize to the extent that intermolecular interactions are maximized. It follows then that the specific volume of a glass depends on the rate of cooling. Fast cooling will not allow molecules to reorganize and attain structures with lower-energy conformations and achieve closer approach of constituent molecules, and thus, \( T_g \) is somewhat higher for faster cooling. Concomitantly, the specific volume is higher for faster cooling. The thermodynamic approach summarized here can be complemented with a kinetic approach nicely discussed elsewhere.

Table 3 presents values of \( T_m \), \( T_g \), and the \( T_g/T_m \) ratio for several organic compounds. The glasses were prepared by very rapid quenching of melts. Compounds that are able to form glasses are not highly symmetric, a property that encourages vitrification. It is noteworthy that no small \( n \)-alkanes are listed; these, with their conformational flexibility, quickly achieve all-trans structures and therefore crystallize even under the most rapid cooling. On the other hand, complete crystallization of linear polyethylene does not typically occur (see below).

As a very general rule of thumb, \( T_g \) is approximately one-half to two-thirds of \( T_m \) (for both in kelvins) for nonpolar or weakly polar molecules, although substantial deviations may be observed for very polar molecules. Organic glasses are metastable in that heating above \( T_g \) (but below \( T_m \)) leads to crystallization. Glasses derived from small organic molecules may have practical utility, such as the glass formed from heating an aqueous solution of sucrose in the presence of glucose or corn syrup (the latter to inhibit crystallization), which makes familiar hard candy. In addition, methylcyclohexane and related glasses have been extensively used for low-temperature spectroscopic studies of isolated single molecules dissolved in the glass.

Many polymeric glasses are readily formed by cooling as a result of the high viscosities of long-chain molecules coupled with a lack of symmetry, and polymer glass formation can also be described by the events outlined in Figure 4. Common examples of polymeric glasses include atactic polystyrene, atactic poly(methyl methacrylate), and polycarbonate.

### CONNECTIONS TO MACROMOLECULAR STRUCTURE–PROPERTY RELATIONSHIPS

We now move to a short discussion of bridges between small molecule structure–property relationships and those of a few polymers.

**Polyethylene**

As noted in our discussion of the data in Figure 2, the \( T_m \) of linear polyethylene, called high-density polyethylene or HDPE,
approaches a limiting value of about 140 °C at molecular weights of about 30,000 g/mol (or about 2150 carbons) and beyond. HDPE and other members of the family, including low-density and linear low-density PE, represent the largest amount of polymers in use today and for the foreseeable future, with numerous applications spanning very high-modulus fibers, packaging and wraps, and gas distribution pipes. However, the use temperatures for all applications are limited by the $T_m$, which is a natural consequence of the segment picture of macromolecules. It should also be noted that HDPE and other PEs are not completely crystalline at room temperature. Segments of the long polymer chains, even segments on the same chain, can begin to crystallize upon cooling from the melt, resulting in the formation of a certain fraction of trapped chain segments between crystallites. Such segments are not able to crystallize and instead have a $T_g$ that is well below room

### Table 3. Glass Transition Temperatures ($T_g$) for a Few Selected Organic Molecules

<table>
<thead>
<tr>
<th>Molecule</th>
<th>$T_m$, K</th>
<th>$T_g$, K</th>
<th>$T_g/T_m$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-methylpentane</td>
<td>119</td>
<td>80</td>
<td>0.67</td>
</tr>
<tr>
<td>methylecyclohexane</td>
<td>146</td>
<td>85</td>
<td>0.58</td>
</tr>
<tr>
<td>toluene</td>
<td>178</td>
<td>112</td>
<td>0.63</td>
</tr>
<tr>
<td>butan-2-ol</td>
<td>298</td>
<td>152</td>
<td>0.34</td>
</tr>
<tr>
<td>1-chloro-2-methylpropane</td>
<td>142</td>
<td>37</td>
<td>0.26</td>
</tr>
</tbody>
</table>

aData from ref 6a.
temperature as a result of the high conformational flexibility and weak intermolecular forces. Therefore, a structure made from HDPE, such as the familiar gallon milk jug, is actually a composite of polyethylene crystallites interconnected with amorphous units.\textsuperscript{10} The low \( T_g \) of the latter gives polyethylene its familiar toughness, and light scattering by the crystallites is responsible for opacity. Theories of polymer crystallization from both solution and the melt remain a vibrant subject of study.\textsuperscript{11}

**Polyesters**

Poly(ethylene terephthalate) or PET is a common polyester used in a variety of applications, including films, beverage bottles, tire cord, and fibers for fabrics. The backbone (Figure 5a) is symmetric enough to allow partial crystallization, with the remainder being glassy at room temperature. PET has a \( T_m \) of about 265 °C. A comparable polyester synthesized from 1,3-propanediol rather than ethylene glycol has a \( T_m \) of about 230 °C, the drop being principally due to the increased flexibility of the chain with the additional methylene and hence a somewhat greater \( \Delta S_m \). A purely aliphatic backbone, exemplified by poly(ethylene adipate) (Figure 5b), has a \( T_m \) of 50 °C due to the high flexibility. Interestingly, a series of aliphatic polyesters with increasing number of methylenes shows the odd–even trend for \( T_m \) as discussed earlier for linear aliphatic hydrocarbons.\textsuperscript{12}

**Polystyrene**

Atactic polystyrene is an extremely important thermoplastic. As the backbone is asymmetric, crystallization does not occur, and polystyrene is completely amorphous with a \( T_g \) of about 100 °C. Hence, disposable polystyrene utensils do not fare well in the hot water of a dishwasher with a temperature uncomfortably close to \( T_g \) and warping occurs easily. It is interesting to consider the dependence of \( T_g \) on molecular weight for atactic polystyrene, as shown in Figure 6. The \( T_g \) is seen to initially increase with molecular weight and then reach a limiting value. The dependence is reminiscent of the plot of \( T_m \) versus number of carbons (and in turn molecular weight) in Figure 2, although the interpretation is somewhat different.

Polymer chain ends, being tethered at only one end, have a greater degree of mobility than segments near the middle of the chain. In other words, the so-called free volume, or “elbow room”, of a chain end is greater. The free volume associated with chain ends decreases with increasing molecular weight simply because the chain end concentration decreases. A point is eventually reached where the concentration of chain ends and the attendant free volume become negligible, and \( T_g \) becomes independent of molecular weight. The dependence of \( T_g \) on molecular weight in Figure 6 typically follows the Flory–Fox equation:\textsuperscript{13}

\[
T_g = T_g(\infty) - c/M_n
\]

where \( T_g(\infty) \) is the limiting \( T_g \) at high molecular weight, \( M_n \) is the number-average molecular weight, and \( c \) is a constant related to the free volume that can be determined from plots of \( T_g \) versus \( 1/M_n \).

In this vein, the \( T_g \) of a multiarm star polystyrene is typically lower than that of a linear one with equivalent molecular weight because of a higher concentration of chain ends in the former.

\begin{figure}

**Figure 5.** Structures of (a) poly(ethylene terephthalate) and (b) poly(ethylene adipate).

\end{figure}

\begin{figure}

**Figure 6.** \( T_g \) vs number-average molecular weight for atactic polystyrene. (Replotted from data in ref 13.)

\end{figure}
CONCLUDING REMARKS

It is hoped that the reader will agree that much can be learned from structure—property relationships of small molecules and that concepts can be immediately translated to an understanding of polymer structure and properties.14,15 The author employs these principles at the outset of introductory-level polymer courses as well as graduate-level courses because of unfamiliarity with key concepts discussed herein. It is also hoped that these concepts can find their way back into discussions in, for example, an introductory organic chemistry course, as older textbooks used to include more detailed sections on physical properties such as boiling points, melting points, and viscosities.16 An intuitive feel for physical properties of organic compounds might broadly enrich such a course while simultaneously preparing students for an appreciation of the factors that dictate the physical properties of synthetic and biological macromolecules.

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Notes

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REFERENCES

(5) Most substances exhibit a decrease in volume at T_m. Water is one of the few common exceptions.
(7) Strictly speaking, this is a temperature range, and it is dependent on the rate of cooling. An appropriate way to remove the dependence of T_g on the cooling rate is to measure T_g as a function of cooling rate and then extrapolate the data to zero cooling rate.
(10) For example, see: Sperling, L. H. Introduction to Physical Polymer Science; Wiley-Interscience: New York, 1986; Chapter 5.
(14) For example, see the current issue of this Journal and a past special issue on polymers: J. Chem. Educ. 1981, 58 (11).

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