

## 1

## Introduction

Polymers are ubiquitous in our daily lives. Natural polymers such as the DNA, RNA, and proteins have played a major role in the evolution of life itself. Cellulose, hemicelluloses, starch (amylose), and other naturally occurring polymers have been studied thoroughly, modified for useful applications and have been the key components of industrial advancement. Familiar to many is the chronological transition of the belief of these substances as colloids to the concept of “polymers.” The “Rise of the Macromolecular Hypothesis” was discussed by Flory [1]. Supporting the Staudinger school of thought were, among others, the X-ray diffraction studies of cellulose by Meyer and Mark [2, 3]. Cellulose is perhaps the first polymer for which oriented X-ray fiber diffraction was recorded [2]. Synthetic polymers have also entered the scene around that time, with the synthesis of polystyrene [4] in 1839.

According to the International Union of Pure and Applied Chemistry (IUPAC) nomenclature [5], the terms polymer and macromolecule do not mean the same thing. A polymer is a substance composed of macromolecules. All macromolecules are not polymers.

### 1.1 Polymer Tacticity

As a polymer (Figure 1.1) is built up of many small molecular monomer units, the dimer (diad), trimer (triad), tetramer (tetrad), pentamer (pentad), and hexamer refer to two, three, four, five, and six monomers, respectively, linked together. Longer sequences of up to about 50-mers are called “oligomers.” However, it is not uncommon in the studies on self-assembly to call such short chains polymers. Although natural or biopolymers such as poly(nucleic acids) (e.g., DNA), proteins and polysaccharides are also long chain molecules, the commonplace notion is that a polymer refers to a polymer refers to the synthetic variety. Of these, vinyl polymers such as polyethylene (PE) and polystyrene are popularly known as plastics. The simplest of polymers is PE, with just a sequence of (CH<sub>2</sub>) units (Figure 1.2). Polymerization of ethylene, vinyl fluoride, vinylidene

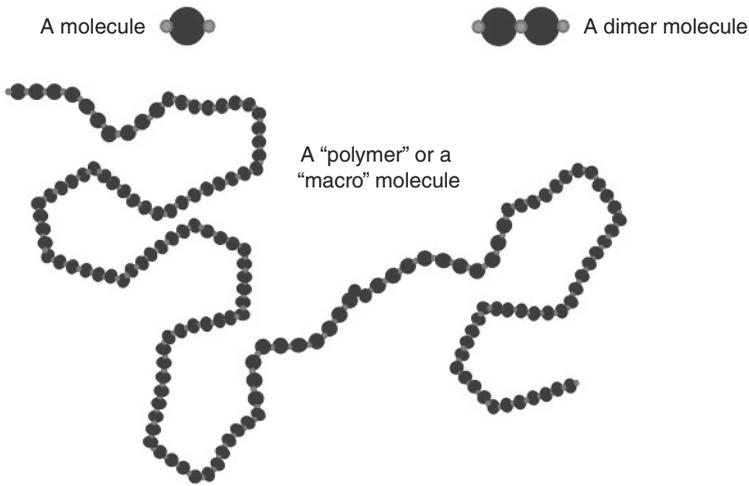


Figure 1.1 Schematics of a monomer, dimer, and a polymer.

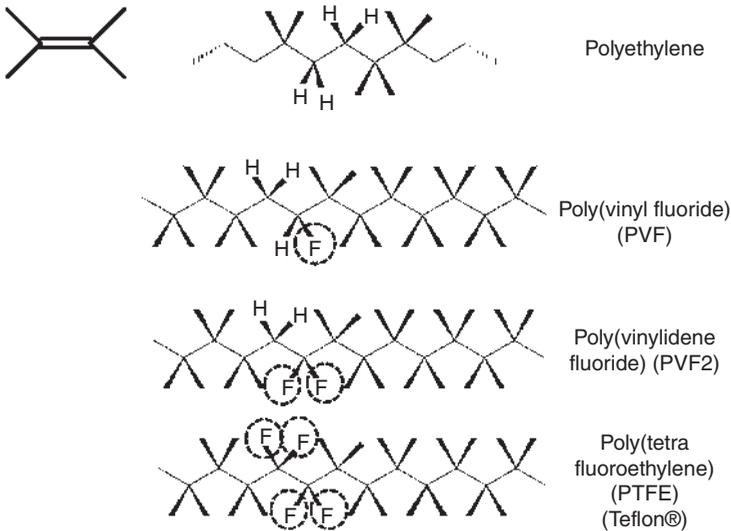
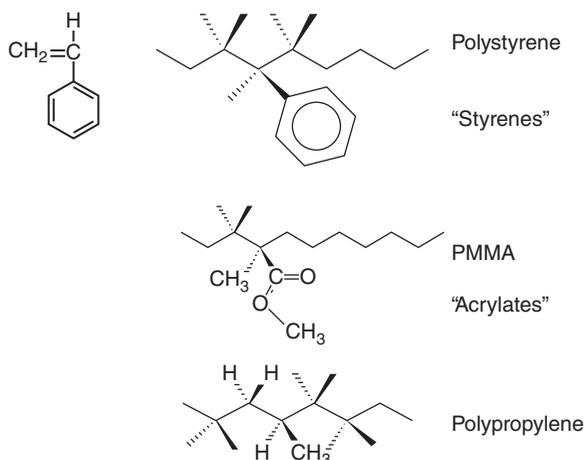


Figure 1.2 Chemical structures of polyethylene and analogous fluorinated polymers. The dashed circles highlight the fluorine atoms.

fluoride, and tetrafluoroethylene lead to PE, poly(vinyl fluoride) (PVF), poly(vinylidene fluoride) (PVF2), and poly(tetrafluoroethylene), respectively. The latter is the well-known Teflon®.

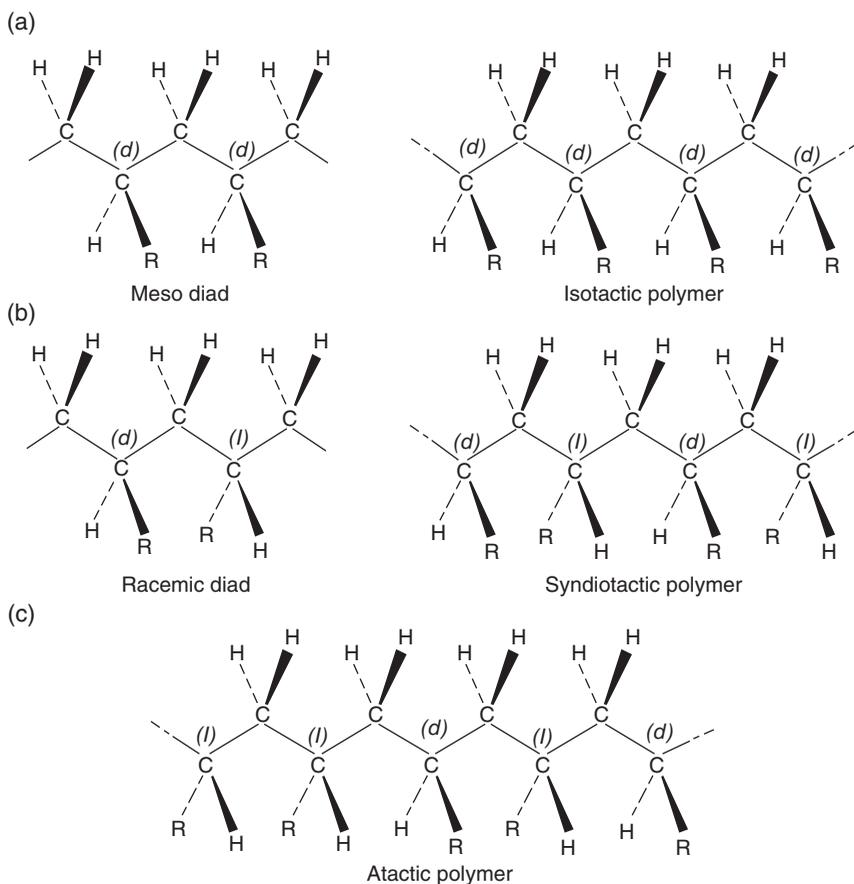
With bulkier substituents, polymers such as polystyrene, poly(methyl methacrylate), and poly(propylene) are obtained (Figure 1.3). Note that in the



**Figure 1.3** Chemical structures of polystyrene, poly(methyl methacrylate), and polypropylene.

case of PE, PVF<sub>2</sub>, and PTFE, the substitution is symmetric, whereas with PVE, polystyrene, PMMA, and polypropylene, it is asymmetric. In the schematics shown in Figures 1.2 and 1.3, the bulkier substituent (R) is shown above the plane of the page. A general rendition is shown in Figure 1.4. In the figure [6], with the skeletal bonds in the all-*trans* conformation, the configuration with R above the page at the asymmetric carbon is designated as *d* and as *l* if it is below. If the substituents on two successive asymmetric carbons are in the same *dd* configuration, it is known as a “*meso*” (*m*) diad.

Perpetuation of such *meso* sequence would lead to an isotactic chain (Figure 1.4a). If the R groups are up and down the page, that is, *dl*, it is the racemic (*r*) diad (Figure 1.4b). The repetition of the racemic diad (*dl* sequence) would result in a syndiotactic polymer. Random occurrence of *m* and *r* results in an atactic polymer. The designation of *d* and *l* for the configuration at the asymmetric carbon is arbitrary. It follows the convention developed by Flory [7], which then led to the formulation of statistical weight matrices to calculate the statistical chain conformations. If the chain is rotated through 180° about a vertical axis such that the ends of the chain are reversed, all the *d* would become *l* and vice versa. But the chain configuration would remain the same as long as the chain ends are indistinguishable. The *ll* would define the meso diad. With the diad configurations *m* and *r* defined earlier, a triad could have sequences of *mm*, *rr*, and *mr* (or *rm*). A tetrad could have sequences *mmm*, *mmr*, *rmr*, *mrmm*, *rrm*, and *rrr*, of which only two of them would lead to stereoregular isotactic or syndiotactic chains. A pentad could have 10 such sequences, 8 of which will be heterotactic. Determining the distribution of such sequences in vinyl polymer chains that were prepared by various synthetic procedures was an active field, concurrent with advances in the NMR

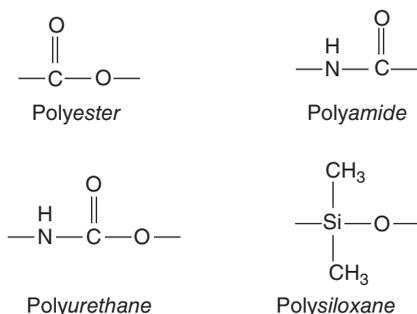


**Figure 1.4** (a)–(c) Schematic of the definition of tacticity for asymmetric chains. (Source: Sundararajan [6]. Reproduced with permission of Springer.)

techniques [8–11]. Although synthetic methods for stereoregular polymers have been developed, some of them such as isotactic polystyrene are of academic interest rather than of commercial use. Atactic polystyrene, in the form of, for example, Styrofoam, finds widespread applications. Likewise, PMMA in its atactic form, is used as a substitution for glass in the form of Plexiglass, as well as in microelectronic chips, etc. Studies on highly isotactic or syndiotactic polymers led to the understanding of aspects such as polymer crystallization and chain folding. In the studies of self-assembly of polymers, tacticity was seldom taken into consideration.

Some of the other polymers commonly used in studies of polymer self-assembly are polyesters, polyamides, polyurethanes, and polysiloxanes, the constituent units of which are shown in Figure 1.5. A summary of the synthetic procedures

**Figure 1.5** Schematics of the segments of polyester, polyamide, polyurethane, and polysiloxane.



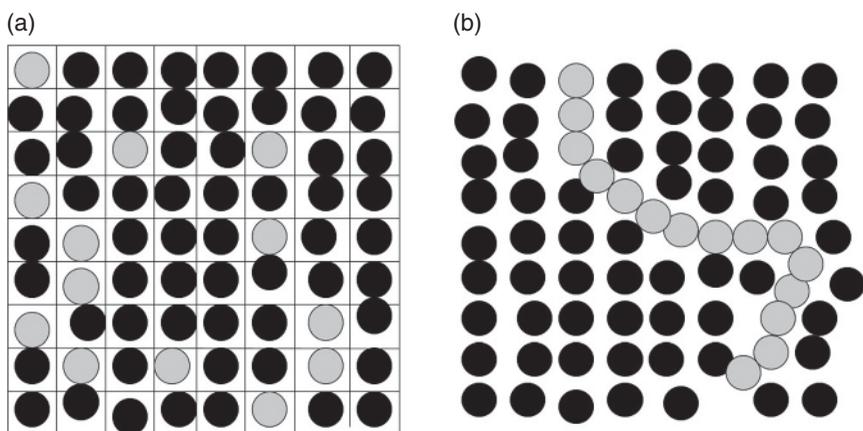
adopted for various types of polymers and their primary characterization properties was given by Sundararajan [6].

## 1.2 Big versus Small

As the small molecule “mono” mer units are joined together to build a “poly” mer, the properties change as the polymer increases in length. For example, ethane has boiling temperature of  $-89^\circ$  and melts at  $-183^\circ\text{C}$ . After growing by a few units, hexadecane melts at  $18.5^\circ\text{C}$ . With a further increase in chain length, triacontane  $[\text{CH}_3-(\text{CH}_2)_{28}-\text{CH}_3]$  melts at  $65^\circ\text{C}$ , and does not boil. High-molecular-weight PE melts at  $138^\circ\text{C}$ . While the small molecules could melt and vaporize, polymer molecules melt and degrade rather than vaporizing. Most polymers show a glass–rubber transition ( $T_g$ ), whereas not all small molecules show a glass transition. Both could crystallize, but polymers should have a regular sequence of monomers (e.g., isotactic or syndiotactic) to be able to crystallize. Those with random sequence remain amorphous. The  $T_g$  is an important property of a polymer since it dictates the processing conditions for industrial applications. Small molecules such as D-glucose have a finite number of conformations, for example, the C1 chair form. However, amylose, which is a high-molecular-weight polymer of D-glucose, could have a large number of conformational sequences between contiguous D-glucose units due to rotations about the interunit  $\text{C}_1-\text{O}-\text{C}_4$  single bonds. The number of accessible conformations without steric overlap determines the “flexibility” of a polymer.

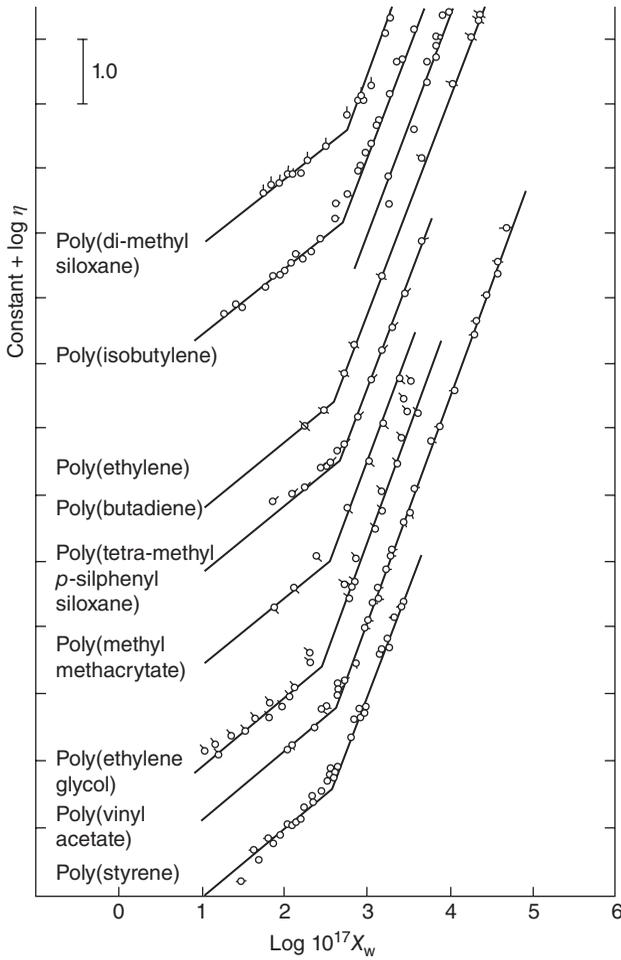
## 1.3 Entanglement

When a small molecule is dissolved in a solvent medium (lattice model) as shown pictorially in Figure 1.6a, both molecules can move and exchange lattice points just by diffusion and thermal motion. However, when a polymer is placed in a solvent (Figure 1.6b), coordinated movement of the monomer units



**Figure 1.6** Schematic of (a) a small molecule and (b) a polymer in a solvent medium. The black circles denote the solvent molecules.

is necessary for the chain to diffuse. This results in loss of entropy of mixing. This would increase the viscosity of the solution compared to the small molecule/solvent mixture. One of the most important properties of a polymer is the “entanglement” between its segments. A small molecule cannot entangle. As the polymer chain grows in length, due to coiling in solution or the melt, entanglement would set in. Most text books would mention a bowl of spaghetti as an example of entangled polymer chains. The polymer must be of a certain minimum length for entanglement to occur. For a bowl of cooked spaghetti to be an entangled stock, the length of the dry noodle should be about one foot. The average length of commercially sold dry spaghetti is 12–14 in., which assures the entanglement upon cooking. The critical molecular weight  $M_c$  for entanglement for polystyrene is about 37 000, while it is only about 5000 g/mol for polycarbonate [12]. Conformational analysis showed that polycarbonate chain can adopt flat helical as well as extended chain shapes with equal probability [13]. Thus, a low molecular weight is sufficient for entanglements to occur in the case of polycarbonate.  $M_c$  varies depending on the polymer structure and conformation. Another parameter is the entanglement molecular weight,  $M_e$ , which corresponds to the average molecular weight between entanglement points. The value of  $M_e$  is usually calculated from the plateau modulus  $G_N^0$  using oscillatory shear experiments. The entanglement plays a significant role in the mechanical properties. Figure 1.7 shows the log–log plot of melt viscosity and molecular weight. It is seen that up to a certain molecular weight, the curve is linear, the region in which the viscosity scales with the first power of molecular weight. Beyond a certain molecular weight, the viscosity increases more sharply, with a slope of 3.4. The point at which the slope



**Figure 1.7** Log-log plot of zero shear viscosities and molecular weight for a number of polymers. For clarity, the curves have been arbitrarily shifted along the ordinate. (Source: Graessley [14]. Reproduced with permission of Springer.)

changes from 1 to 3.4 is the one corresponding to  $M_c$ . The following relationship generally applies to most linear polymers:

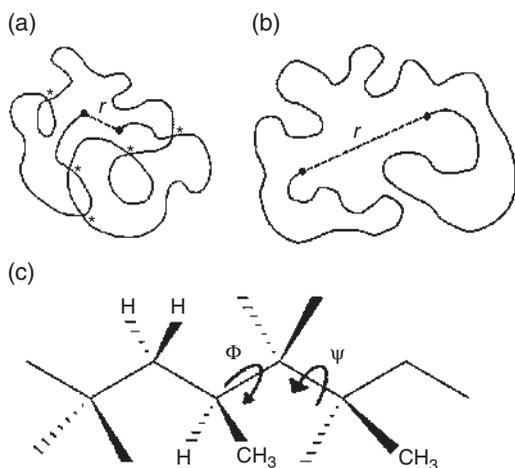
$$\eta = KM \quad M < M_c \quad (1.1)$$

$$\eta = K'M^{3.4} \quad M > M_c \quad (1.2)$$

Here,  $K$  and  $K'$  are constants.

## 1.4 Excluded Volume

In the conceptual framework of theoretical treatment of polymer chains, models such as freely jointed and freely rotating have been used. In the freely jointed or random walk model, a chain with a series of bonds each of length  $l$  can adopt any (bond) angle between them, any dihedral angle and cross each other. There is no restriction on the contour of the chain except that the length of each step (bond) is fixed. Such a chain is “unperturbed” by any restrictions. In the freely rotating model, the bond lengths and bond angles are fixed, but the chain can assume any torsion angle between bonds. Now the chain is perturbed by imposing the condition that the bond angle is restricted to a certain value. In a real chain, the bonds cannot cross each other, that is, occupy the same space, which results in “excluded volume,” as illustrated in Figure 1.8a. We find the concept of excluded volume in real life everywhere. If someone is sitting on a park bench or in a seat in a movie theater, that volume of space is “excluded” for others. In a hypothetical chain shown as in Figure 1.8a, the chain segments (bonds) are allowed to cross each other (indicated by \*), as in the case of freely jointed model. Since the excluded volume would prevent such overlap, the chain would expand as in Figure 1.8b and the end-to-end distance  $r$  would increase. Another factor to consider is that the range of sterically accessible dihedral angles, illustrated in Figure 1.8c, between any two monomers would be restricted to various degrees depending on the type of polymer and the



**Figure 1.8** (a) A random coil with long-range interaction (excluded volume overlap, denoted by \*) between segments which are close in space but with large separation in the sequence along the chain. This would be the case in a freely jointed chain. (b) The chain expands to relieve the excluded volume overlap. The end-to-end distance  $r$  increases compared to that in (a). (c) Illustration of dihedral angles  $\Phi$  and  $\Psi$  between contiguous units in a chain. (Source: (a) and (b) Tonelli [15]. Reproduced with permission of Wiley.)

interactions between contiguous monomers. These are short-range interactions which occur between contiguous neighbors, and are determined by the bond angles, torsion angles, and nonbonded forces such as van der Waals, hydrogen bonding, etc. Thus, the random coil of a real chain would be more expanded than the hypothetical free jointed or freely rotating models.

The role of excluded volume in the solution conformations of polymers has been discussed in detail by Flory [1]. As mentioned earlier, the long-range interaction gives rise to the excluded volume effect and causes chain expansion. The “long range” here does not mean in terms of the physical distance between the segments but the relative positions of the segments in the sequence along the chain, for example, the 5th and the 100th monomer unit, when they come close to each other. The average conformation of a randomly coiled chain in solution is governed by the short- and long-range interactions as well the polymer–solvent interaction. In a good solvent, the polymer–solvent interaction would be stronger than the mean of the energies between the polymer–polymer and solvent–solvent pairs. The chain would tend to expand to maximize the contacts between the polymer segments and the solvent molecules. In a poor solvent, the polymer would tend to adopt compact conformations to increase the number of contacts between the intrapolymer segments (subject to excluded volume effects) and to minimize the polymer–solvent interaction. In a particular solvent, at a certain temperature, the expansion due to excluded volume may be compensated exactly by the contraction due to the poor solvent. At this temperature, a balance occurs between the excluded volume (mutual volume exclusion of the segments), which expands the chain and the positive energy of mixing in the solvent which promotes first-neighbor contacts between the polymer segments resulting in a compact conformation. This temperature is known as the Flory  $\Theta$  temperature. The chain would be unperturbed by long-range interactions and its conformation would be governed by short-range interactions between contiguous neighbors. By taking the rotations  $\Phi$  and  $\Psi$  marked in Figure 1.8c to be discrete conformational states such as *trans*, *gauche*, and *gauche minus* (*t*-, *g*-, and *g-rotational isomers*, respectively), Flory [7] introduced the rotational isomeric-state treatment of the statistical chain conformations in the unperturbed state (i.e.,  $\Theta$  condition). The  $\Theta$  temperature depends on the solvent–polymer pair. Measurements and calculations of the  $\Theta$  temperatures and chain dimensions for various polymers were a significant activity during the 1960s, extending to even the 1990s. The characteristic ratio of the unperturbed end-to-end distance of a chain with infinite molecular weight, defined as

$$C_\infty = \frac{\langle r^2 \rangle_0}{nl^2} \quad (1.3)$$

was related to the experimental measurements at the  $\Theta$  temperature [7]. It was also during this period that experimental (neutron scattering, deuterated polymers, etc.) and theoretical work confirmed that the chain conformation in the amorphous,

glassy state corresponded to that in the  $\Theta$  condition. Properties such as the entanglement molecular weight ( $M_c$ ), distance between entanglements ( $M_e$ ), and viscoelastic properties have been correlated to the characteristic ratio [16–20]. A collection of the experimental results on the theta temperatures for various solvent/polymer pairs and the chain conformations was published [21] in 2007.

## 1.5 Free Volume

The excluded volume concept discussed earlier relates to the chain conformation and the physical properties associated with it. Another important factor is the “free volume,” which is related to the glass transition temperature of a polymer. This is similar to the void space between spheres that are packed in a container. As the polymer coils pack themselves in space, intermolecular steric repulsions as well as thermal motions create free volume in a polymer matrix. The free volume would then depend on the temperature as well as the ease with which the chain can change its shape (conformation). For example, the rotational states of contiguous units of a poly(dimethyl siloxane) (PDMS) chain encounter very little energy barrier and the chain is hence highly flexible. As the temperature is lowered, the chain motion would cease at a particular temperature, which is the  $T_g$ . Due to its high conformational flexibility, the molecular motion in the case of PDMS does not freeze until a very low temperature of  $-125^\circ\text{C}$ . For atactic polystyrene, the  $T_g$  is about  $100^\circ\text{C}$ ; for poly(arylene sulfone), it is  $250^\circ\text{C}$ . Thus, the free volume above  $T_g$  depends on the conformational flexibility, and interchain interactions. Main chain aromatic polymers in which  $\pi$ - $\pi$  interaction is possible and those with interchain hydrogen bonds (e.g., polyamides) exhibit high glass transition temperatures. Other features that influence the  $T_g$  are long side chains, tacticity, etc. The molecular weight distribution would also affect the free volume. If the bulk sample has a large number of short chains in its midst, the number of chain ends would be significant. Since there must be a certain steric space between these chain ends, the free volume would increase, and the  $T_g$  would decrease. The low-molecular-weight fractions would act as internal plasticizers. The same would occur if the polymer is exposed to a solvent vapor or if a small-molecule plasticizer is added. These would have a lubricating effect enabling chain movement and increase the free volume. The effect of free volume on the self-assembly of small molecules in polymer matrices is discussed in Chapter 8.

## 1.6 Self-Assembly

The research related to “self-assembly” spans a wide range of areas. It is believed to have originated with the studies on biological systems such as the DNA and RNA that led to an understanding that mutual recognition between

molecular segments enables them to associate with one another. It is interesting to note the ever-increasing interest in this area, as shown in Table 1.1. These numbers were obtained from a search of the SciFinder Scholar (Chemical Abstracts Service of the American Chemical Society).

The search term was “self-assembly,” with no other filter except the range of years. Thus these numbers include publications in all languages as well as patents, on not only molecular but also colloidal and other component self-assembly. While there were just a few articles in the 30-year period from 1960 to 1990, the number increased dramatically since then. It might be that it was during the late 1990s and the 2000s that the idea of using self-assembled systems for nanotechnology was gaining momentum.

Pelesko [22] quoted definitions of several authors as to the meaning of self-assembly. It is now generally defined as a process by which molecules or parts of molecules *spontaneously* form organized structures driven by specific *non-covalent* interactions between themselves, without an external stimulus. Further, the static self-assembly is a situation where the ordered state leads to equilibrium structures such as crystals. Although organized structures such as crystallization could occur in a large number of systems, the self-assembly is characterized by *spontaneous* and *reversible* organization of the molecular components. When the components are molecules, it is “molecular self-assembly.” Whitesides [23, 24] presented scenarios of making useful devices at various length scales by self-assembly. Pelesko [22] discussed the self-organization of colloidal and other particle systems by the application of electrostatic force.

**Table 1.1** Number of publications from SciFinder Scholar on “self-assembly” as entered and the “concept of self-assembly.”

Publication years	Self-assembly	Concept of self-assembly
1960–1964	0	5
1965–1969	43	65
1970–1974	76	111
1975–1979	204	280
1980–1985	402	591
1986–1990	491	838
1991–1995	1 612	3 441
1996–2000	6 167	12 960
2001–2005	19 319	34 351
2006–2010	39 639	63 411
2011–2015	60 011	87 474
Total	<b>127 964</b>	<b>203 527</b>

The self-assembly can thus be “directed” by specific external fields. Grzelczak et al. [25] reviewed the process and applications of directed self-assembly of nanoparticles. The term self-assembly has been used even in assemble-it-yourself furniture systems, where the assembly is modular [26, 27].

Although the majority of studies of self-assembly focus on functionalizing molecules with codes for hydrogen bonding,  $\pi$ -interaction or Coulombic interactions, other factors such as hydrophobic or solvo-phobic interactions also play a role in self-assembly. For example, phthalocyanines and porphyrins are insoluble in most organic solvents, but they could be made soluble in common solvents such as chloroform by peripheral substitution. Addition of a nonsolvent to such solutions in a controlled manner would trigger phase separation and the self-assembly via  $\pi$ -interaction, leading to nanowires and similar morphologies [28]. Even when a molecule is coded with, for example, hydrogen bonding, mutual steric and geometric registry must be favorable for self-assembly to occur.

## 1.7 Polymer Self-Assembly

As for the self-assembly of polymers, those with hydrogen bonding groups, such as polyamides, with aromatic interactions, for example, polyaramids, have been studied extensively in the past. As shown in Figure 1.5, the amide segment is similar to the amino acid moiety. Similar to the trend shown in Table 1.1, the research activity in the area of polymer self-assembly became intense only in the late 1990s. Table 1.2 shows the results of a search of the SciFinder Scholar. Although studies on hydrogen bonded polymers and similar systems were active before the 1990s, they do not appear significantly in the table, perhaps because the words “self-assembly” did not gain fame at that time in the area of synthetic polymers. In attempts to understand the molecular recognition between the nucleic acid base pairs, synthetic analogues were synthesized a few decades ago [29–39]. To this end, vinyl polymers of the nucleic acid bases, poly(vinyl adenine), poly(vinyl cytosine), poly(vinyl uracil), and poly(vinyl thymine), were synthesized and their interactions were studied since the 1970s.

Most articles on molecular self-assembly would point to the molecular recognition in biological molecules and suggest that Nature should be imitated when designing novel materials. To quote Ronald Breslow [40], “We learned the principle of wings from the birds but not the details of how to use them and power the flight. We take the principles of Nature, not the blueprint. The jumbo jet is not a scaled up version of the pigeon.”

In considering self-assembly as it relates to polymers, the aspects are the self-assembly of polymers themselves and the self-assembly of individual units to create a polymer. In the former case, the polymer self-assembly could be

**Table 1.2** Number of publications from SciFinder Scholar on “polymer self-assembly” as entered and the “concept of polymer self-assembly”

Publication years	Polymer self-assembly	Concept of polymer self-assembly
1960–1964		
1965–1969		
1970–1974		3
1975–1979		8
1980–1985		18
1986–1990		39
1991–1995	7	275
1996–2000	25	1204
2001–2005	93	3370
2006–2010	182	6250
2011–2015	215	9191
	<b>522</b>	<b>20358</b>

driven by association elements such as hydrogen bonds. The self-association in the case of block copolymers would be driven by the incompatibility of the segments and to some extent by “self-recognition,” “self-sorting.” Using the principles of Nature, polymers functionalized with specific recognition units have been designed [41–48], and these led to various potential applications in areas such as nanotechnology. Using such methodologies to create folded structures, intramolecular and intermolecular association of chromophores with oligomeric or polymeric linkages by chain folding have created opportunities for optical applications [49–52]. We will discuss some of these in the following chapters.

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