# 1
Introduction

1.1
Metal-Containing Polymers

Carbon is not a particularly abundant terrestrial element, ranking 14th among those in the Earth's crust, oceans, and atmosphere. Nevertheless, carbon-based or organic macromolecules form the basis of life on our planet, and both natural and synthetic macromolecules based on carbon chains are ubiquitous in the world around us. Organic polymers are used as plastics, elastomers, films, and fibers in areas as diverse as clothing, food utensils, car tires, compact discs, packaging materials, and prostheses [1]. Moreover, with the additional impetus provided by the Nobel prize winning discovery of electrical conductivity in doped polyacetylene in the mid-1970s, exciting new applications in electroluminescent and integrated optical devices and sensors are also now under development [2–6]. The remarkable growth in the applications of organic polymeric materials in the latter half of the 20th century can mainly be attributed to their ease of preparation, and the useful mechanical properties and unique propensity for fabrication that are characteristic of long-chain macromolecules. Their ease of preparation is a consequence of the highly developed nature of organic synthesis, which, with its logical functional group chemistry and ready arsenal of metal-catalyzed reactions, allows a diverse range of carbon-based polymers to be prepared from what are currently plentifully available and cheap petroleum-derived monomers [7, 8]. In the late 20th century, organic polymer science has been further advanced by the creation of remarkable polymer architectures such as block copolymers, star polymers, and tree-like molecules or *dendrimers*, which are attracting intense attention.

In contrast to the situation in organic chemistry, the ability to chemically manipulate atoms of inorganic elements is generally at a much more primitive stage of development. Even seemingly simple small inorganic molecules can still be surprisingly elusive, and the formation of bonds between inorganic elements is still often limited to salt metathesis processes. Inorganic analogues of readily available multiply-bonded organic monomers such as olefins and acetylenes, for example, are generally rather difficult to prepare. The development of routes to polymer chains of substantial length constructed mainly or entirely from inorganic elements has therefore been a challenge. Indeed, apart from the cases of polysiloxanes (**1.1**) [9, 10], poly-
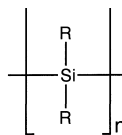
phosphazenes (**1.2**) [9, 11–13], and polysilanes (**1.3**) [9, 14, 15], this area has only been significantly expanded since the 1980s and 1990s [8].
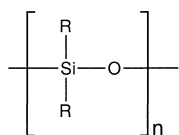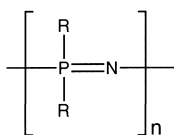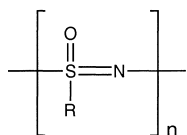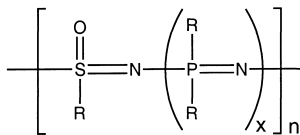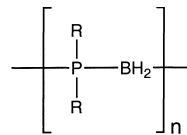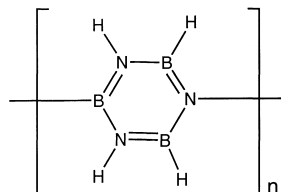

In the case of polymers based on non-metallic main group elements, the development of novel thermal, Lewis acid or base promoted, or transition metal-catalyzed polycondensation strategies that proceed with the elimination of small molecules such as $Me_3SiOCH_2CF_3$, Me_3SiCl, H_2, H_2O, and CH_4, as well as the discovery of ring-opening polymerization (ROP) and related processes, has permitted improved approaches to existing polymer systems (e.g. **1.2** and **1.3**) [16–25] and access to new materials. Examples of the latter include polyoxothiazenes (**1.4**) [26], polythionylphosphazenes (**1.5** and **1.6**) [27–29], polyphosphinoboranes (**1.7**) [30], polyborazylenes (**1.8**) [31], and other systems that contain boron-nitrogen rings such as polycyclodiborazanes (**1.9**) [32].
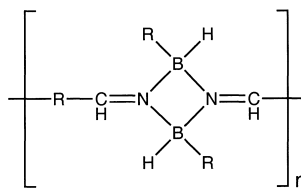

Many similar synthetic challenges exist in the area of polymers based on metallic elements. At the molecular level, metal chemistry is well developed. For example, the preparation of carefully designed, single-site transition metal catalysts has already had a dramatic impact on polymer science, particularly for the polymerization

of alkenes [33]. Inorganic solid-state materials chemistry has also now been developed to the extent that scientists are able to exploit the vast range of possibilities arising from the chemical diversity made available throughout the Periodic Table [34–36]. The creation of high-temperature ceramic superconductors, state-of-the-art magnetic, electrochromic, or electrooptical materials, and unprecedented catalysts with controlled porosity, are all consequences of chemists' now highly impressive ability to organize atoms of inorganic elements in two and three dimensions. In contrast, the elaboration of efficient synthetic routes to metal-containing polymers has been the real roadblock to the development of 1-D analogues of the well-established 2-D layered and 3-D metal-containing solid-state materials. This is particularly the case if the metal atoms are located directly in the main chain, where they are most likely to exhibit the most profound influence on the properties of the macromolecular material. Over the last decade of the 20th century, there have been clear indications that this synthetic problem is being productively tackled and a wide variety of intriguing new polymer systems have emerged. These developments are the subject of this book, which is written both to review the state-of-the-art and also to further help stimulate both fundamental and applied research in this exciting area that is ripe for exploitation and full of future potential.

1.2
Fundamental Characteristics of Polymeric Materials

Polymers exhibit a range of architectures and unique properties, the study of which represents a major core area of polymer science. Although this book assumes that the reader is familiar with some of the basic concepts of polymer science, such as the structures of common macromolecular materials (polystyrene, polyisoprene, etc.), additional knowledge is certainly desirable for an appreciation of much of the research described and the challenges for the future. In this section, we briefly cover some key points for the benefit of readers unfamiliar with the areas that are relevant to the discussions in subsequent chapters. For detailed background material the reader is referred to the many excellent introductory and advanced books on polymer science and the recent literature cited in this section [7, 37–42].

1.2.1
Polymer Molecular Weights

Samples of synthetic polymers are generally formed by reactions where both the start and end of the growth of the macromolecular chain are uncontrolled and are relatively random events. Even chain-transfer reactions, where, for example, one polymer chain stops growing and in the process induces another to begin, are prevalent in many systems. Synthetic polymer samples, therefore, contain molecules with a variety of different chain lengths and are termed *polydisperse*. For this reason, the resulting molecular weight distribution is characterized by an *average molec-*

ular weight. The two most common are the *weight-average molecular weight*, M_w, and the *number-average molecular weight*, M_n. The quantity M_w/M_n is termed the *polydispersity index* (PDI), which measures the breadth of the molecular weight distribution and is ≥ 1. In the case where the polymer chains are of the same length $M_w = M_n$ (i.e. PDI = 1), the sample is termed *monodisperse*. Such situations are rare, except in the case of biological macromolecules, but essentially monodisperse systems also occur with synthetic polymers where the polymerization by which they are prepared is termed *living*. In such cases, initiation is rapid and no termination or chain-transfer reactions occur; under such conditions, the polymer chains initiate at the same instant and grow until the monomer is completely consumed, resulting in macromolecular chains of the same length [7]. In practice, living systems are not perfect; for example, very slow termination reactions generally occur. This leads to polymer samples which are of narrow polydispersity (1.0 < PDI < 1.2) rather than perfectly monodisperse (PDI = 1.0). Living systems are of particular interest because they allow the formation of controlled polymer architectures. For example, unterminated chains can be subsequently reacted with a different monomer to form block copolymers.

A variety of different experimental techniques exist for the measurement of M_w and M_n [38–41]. Some afford absolute values, while others give estimates that are relative to standard polymers, such as polystyrene, which are used as references. One of the simplest techniques for obtaining a measurement of the molecular weight of a polymer is Gel Permeation Chromatography (GPC) (also known as Size Exclusion Chromatography, SEC). This method affords information on the complete molecular weight distribution as well as values of M_w and M_n (and hence the PDI). Unfortunately, the molecular weights obtained are relative to that of the polymer standard used to calibrate the instrument unless special adaptations of the experiment are made or standard monodisperse samples of the polymer under study are also available as references. Light-scattering measurements are generally time consuming but permit absolute values of M_w to be obtained and also yield a wealth of other information concerning the effective radii of polymer coils in the solvent used, polymer-solvent interactions, and polymer diffusion coefficients. The introduction of light-scattering detectors for GPC instruments has now made it possible for both absolute molecular weights and molecular weight distributions to be determined routinely. It should also be noted that mass spectrometry techniques such as Matrix-Assisted Laser Desorption Ionization – Time of Flight (MALDI-TOF) have now been developed to the stage where they are extremely useful for analysis of the molecular weights of polymers and can give molecular ions for macromolecules with molecular weights substantially greater than 100,000.

Although most polymer samples possess a single molecular weight distribution by GPC and are termed *monomodal*, for some the molecular weight distribution actually consists of several individual, resolvable distributions. In such cases, the molecular weight distribution is referred to as *multimodal*. For example, if a high and a low molecular weight fraction can be distinguished then the distribution is termed *bimodal* (Fig. 1.1a). Examples of broad and narrow monomodal molecular weight distributions are shown in Fig. 1.1b and 1.1c, respectively.

a)

b)

c)
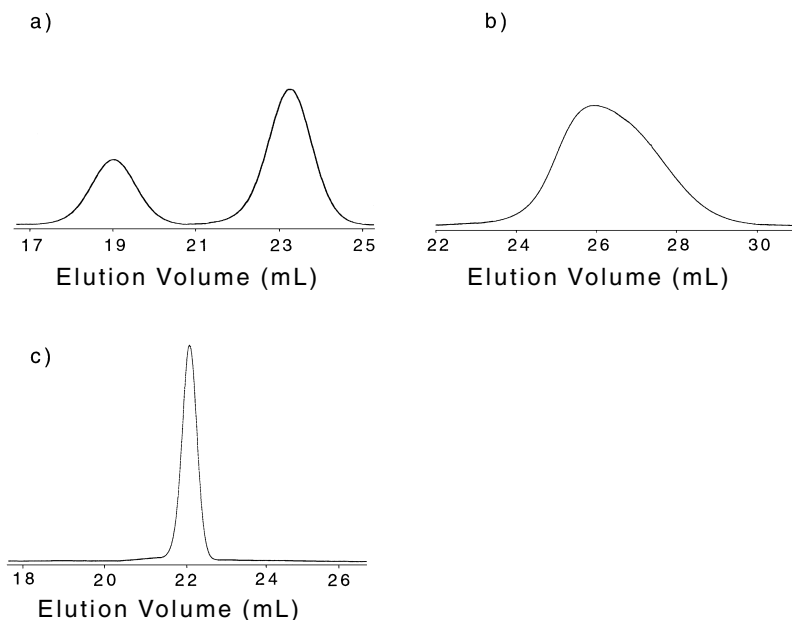
Fig. 1.1 Typical GPC traces showing (**a**) a bimodal molecular weight distribution, (**b**) a broad monomodal molecular weight distribution (PDI=2.3), and (**c**) a narrow monomodal molecular weight distribution (PDI=1.05). The *x*-axis shows the elution volume for the GPC instrument with molecular weight increasing from right to left.

1.2.2
Amorphous, Crystalline, and Liquid-Crystalline Polymers: Thermal Transitions

As polymer chains are usually long and flexible, they would be expected to pack randomly in the solid state to give an amorphous material. This is true for many polymers, particularly those with an irregular chemical structure. Examples are the stereoirregular materials *atactic* polystyrene (**1.10**) and *atactic* polypropylene (**1.11**), in which the Ph and the Me substituents, respectively, are randomly oriented.
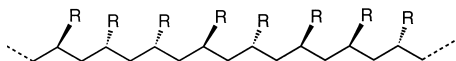
1.10 R = Ph
1.11 R = Me

However, polymer chains that have regular structures can pack together in an ordered manner to give crystallites. In general, perfect single crystals are not formed by long polymer chains for entropic reasons, and such materials are therefore often more correctly referred to as *semicrystalline*, as amorphous regions are
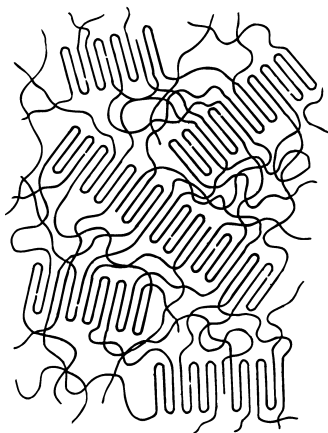
**Fig. 1.2** Model of a semicrystalline polymer showing chain-folded crystallites embedded in an amorphous matrix (Reproduced from [37a]).

also present [43]. At the edges of the crystallites, the macromolecular chains fold and re-enter the crystal. The manner in which this occurs has been a subject of much debate in the polymer science community, but a reasonable picture of the amorphous and crystalline regions of a semicrystalline polymer is shown in Fig. 1.2. Information on the morphology of polymers is revealed by techniques such as powder X-ray diffraction (PXRD), which is often called wide-angle X-ray scattering (WAXS) by polymer scientists, and small-angle X-ray scattering (SAXS). The crystallites exist in a polymer sample below the *melting temperature* (T_m), an order-disorder transition, above which a viscous melt is formed.

The presence of crystallites can lead to profound changes in the properties of a polymeric material. For example, crystallites are often of the appropriate size to scatter visible light and thereby cause the material to appear opaque. They often lead to an increase in mechanical strength, but also to brittleness. Gas permeability generally decreases, as does solubility in organic solvents as an additional lattice energy term must be overcome for dissolution to occur. Examples of crystalline polymers are the stereoregular materials *syndiotactic* polystyrene (**1.12**), in which the orientation of the Ph groups alternates in a regular manner, and *isotactic* polypropylene (**1.13**), in which the Me groups have the same orientation. This structural regularity allows the polymer chains to pack together in a regular manner as crystallites.


1.12

1.13
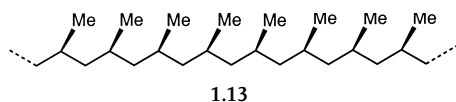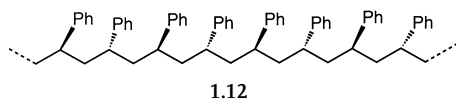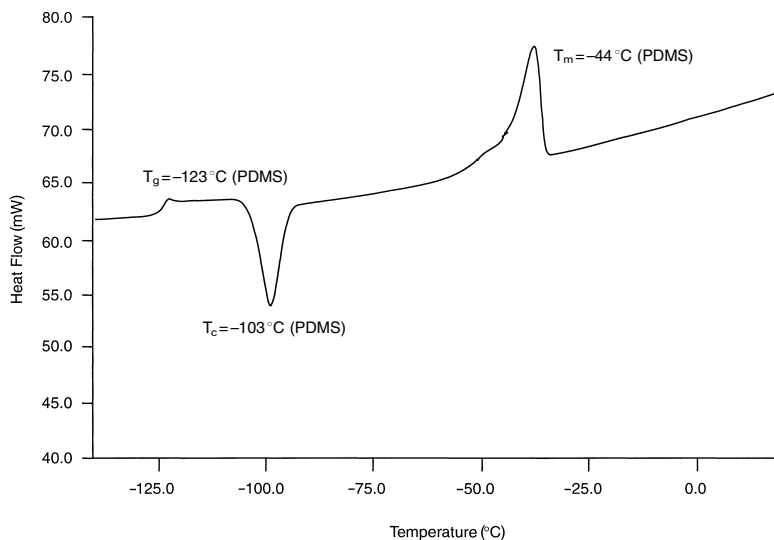
Fig. 1.3 A DSC trace showing a series of idealized thermal transitions (i.e. T_g, T_m, and T_c) for poly(dimethylsiloxane) (PDMS).

In addition to the melting temperature (T_m), which arises from the order-disorder transition for crystallites in a polymer sample, amorphous regions of a polymer show a *glass transition* (T_g). This second-order thermodynamic transition is not characterized by an exotherm or endotherm, but rather by a change in heat capacity, and is related to the onset of large-scale conformational motions of the polymer main chain. Generally, stiff polymer chains and large, rigid side groups generate high T_g values. Below the T_g an amorphous polymer is a glassy material, whereas above the T_g it behaves like a viscous gum, because the polymer chains can move past one another. By linking the polymer chains together through cross-linking reactions, rubbery elastomers can be generated from low T_g polymers. Purely amorphous polymers such as atactic polystyrene show only a glass transition ($T_g \approx 100\,°C$), whereas semicrystalline polymers show both a T_m and a T_g. Semicrystalline polymeric materials are rigid plastics below the T_g and become more flexible above the T_g. Above the T_m, a viscous melt is formed.

It is noteworthy that the rate of polymer crystallization can be extremely slow and polymers that can potentially crystallize are often isolated in a kinetically stable, amorphous state. The polyester poly(ethylene terephthalate) (**1.14**) provides a good example. This material has a T_g of $69\,°C$ and a T_m of $270\,°C$, but crystallization only becomes rapid well above the T_g. Rapid cooling from the melt yields an amorphous material, whereas slow cooling or annealing above the T_g can yield percentage crystallinities up to 55% [38]. A potentially crystallizable polymer that is in an amorphous state can show an exothermic *crystallization transition* (T_c) at elevated temperatures. The thermal transitions of a polymer are commonly investigated by the technique of differential scanning calorimetry (DSC). A typical DSC trace showing a T_g, a T_c, and a T_m is shown in Fig. 1.3.
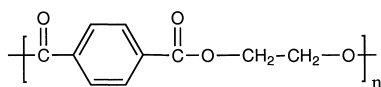
1.14

Polymers can also exhibit *liquid crystallinity*, a fluid state in which some long-range positional or orientational order, or a *mesophase*, exists [43, 44]. This arises when significant shape anisotropy is present in the polymer main chain or side-group structure. Liquid crystallinity can exist in the bulk material, where the mesophase is formed over a certain temperature range (*thermotropic*), or as a consequence of a preferred arrangement of polymer molecules in solution above a certain concentration (*lyotropic*). Thermotropic liquid-crystalline materials show a mesophase between a *melting temperature for the crystalline phase* (T_{lc}) and the *clearing temperature* (T_{cl}), above which an isotropic melt is formed. The order present in liquid-crystalline polymers can be used to broadly classify the materials as *nematic* (order in only one dimension) or *smectic* (weakly layered), as illustrated for the case of a main-chain liquid-crystalline polymer that consists of rigid and flexible segments (Fig. 1.4a and b, respectively). Many permutations on this theme are possible, as illustrated in Fig. 1.4c to g [43, 44]. Liquid-crystalline polymers can be analyzed by polarizing optical microscopy, where the ability of mesophases to influence the plane of polarized light yields various textures, which are used to characterize the materials. Liquid-crystalline polymers are of considerable interest as high-performance materials and have potential uses in photonics and data storage.
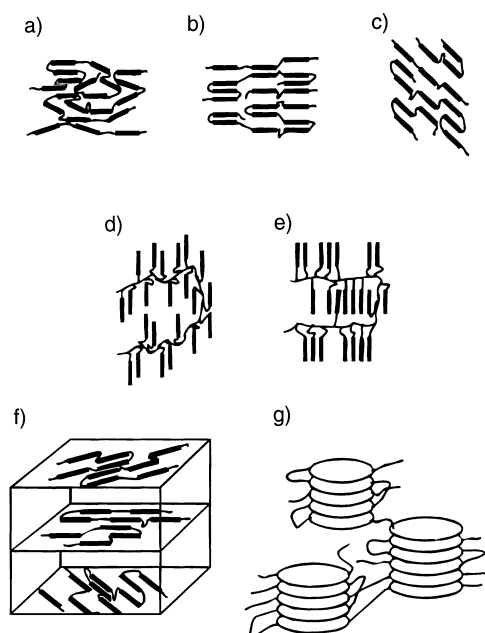
Fig. 1.4 Nematic and smectic main-chain liquid-crystalline polymers: (**a**) main-chain nematic, (**b**) main-chain smectic A, (**c**) main-chain smectic C, (**d**) side-chain nematic, (**e**) side-chain smectic A, (**f**) main-chain cholesteric, (**g**) main-chain discotic (Reproduced from [43]).

1.2.3
Polymers versus Oligomers: Why are High Molecular Weights Desirable?

Two related questions that are often asked are the following: "How long does a molecule have to be in order for it to be called a polymer rather than an oligomer?" and "Why are high molecular weights desirable?" Indeed, the electronic and optical properties of extended conjugated molecular structures are often maximized at chain lengths of 30 chain atoms or so. So why are longer chains needed? The main reasons for the widespread use of polymers are their excellent mechanical properties such as strength, deformability, and elasticity. Simple considerations allow a rough estimation of the substantial chain lengths necessary to obtain these properties.

In crystalline polymers, the need is for polymer molecules that function as "tie molecules" which are long enough to connect individual crystallites (see Fig. 1.2). This leads to strong covalent bond connections both within the crystallites and also between them, and thereby enhances mechanical strength. Typically, chains must consist of at least 100 chain atoms for such connections to be possible. For a monomer of molecular weight 100, this corresponds to $M_n \approx 10,000$. In amorphous polymers, the chains need to be long enough for entanglement to take place (Fig. 1.5). Chain entanglements help the material to maintain structural integrity under stress. The onset of significant chain entanglement, the *weight-average critical entanglement chain length* $Z_{c,w}$, can be determined from melt viscosity measurements and generally corresponds to ca. 600 chain atoms. For poly(dimethylsiloxane), $Z_{c,w}=630$, which corresponds to $M_w \approx 23,000$, whereas for polystyrene $Z_{c,w}=600$, which corresponds to $M_w \approx 31,000$. These molecular weights therefore represent the low end for the useful mechanical properties of these polymers [39]. Clearly, the molecular weight required for useful mechanical properties depends on the particular polymer being considered.

The need for high molecular weights in order to obtain useful mechanical properties is neatly illustrated by a comparison of straight-chain hydrocarbons. It is easy to appreciate the difference between a birthday candle (a mixture of C_{25}–C_{50} alkanes, i.e. $M_n \approx 500$), which is a brittle material and breaks easily, and a polyethylene wash bottle tip (chains of >1000 carbon atoms, i.e. $M_n > 15,000$), which can be repeatedly bent [39].

It is obvious, then, that high molecular weight polymers have major advantages over low molecular weight analogues for most applications. However, it is important to note that exceptions to this rule exist. For example, in applications as toner particles in laser printing and xerography, where low melting points are impor-

a) b)
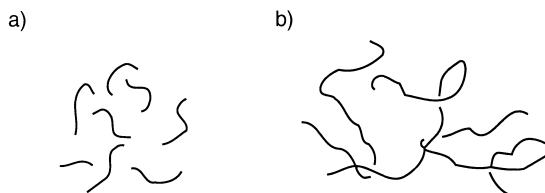
Fig. 1.5 **(a)** Oligomers, which do not entangle due to their short chains, and **(b)** chain entanglements in an amorphous high molecular weight polymer.

tant, low molecular weight materials are actually desirable. In addition, for certain electronics applications, well-defined monodisperse oligomers (e.g. the linear hexamer sexithiophene) can have better defined and more predictable electronic and optical properties. In such cases, the lower processability of the oligomer can be circumvented by the use of vacuum deposition to form high quality films. Relatively low molecular weight polymers are also useful as precursors to ceramic materials. For example, after fabrication into fibers, pyrolysis can yield a ceramic product in high yield. In such applications, sufficient viscosity for spinning into fibers and high ceramic yield are of great importance. Nevertheless, in the vast majority of cases, high molecular weights allow more desirable material properties. In this book, then, we will make a broad generalization and use the term "polymer" to refer to materials with $M_n > 10,000$, and will use the term oligomer to refer to materials of lower molecular weight.

1.2.4
Polymer Solubility

Films of polymeric materials are readily fabricated from solution by evaporation- or dip-casting and by spin-coating techniques. However, polymers generally show a lower tendency to dissolve in solvents compared to molecular compounds for thermodynamic reasons. This is a consequence of the fact that the *entropy of dissolution*, ΔS_{diss}, is substantially reduced for a macromolecular material relative to that for a small molecule compound. In solution, the additional disorder for a polymer chain compared to that present in an amorphous polymeric solid is very small, especially if the main chain is rigid (i.e. the T_g is high). The polymer segments in solution are still constrained to one dimension and so the amount of "disorder" is not vastly different from the situation in the solid state. By contrast, small molecules possess considerably more translational freedom in solution compared to the solid state, as motion in three different dimensions is possible. The thermodynamic polymer solubility problem becomes particularly acute if the polymer is crystalline, as an unfavorable lattice enthalpy term ΔH_{cryst} must also be overcome for dissolution to occur. Thus, the choice of a solvent that has favorable interactions with a polymer becomes critical when dissolution of the polymer is desired. The attachment of long flexible organic substituents (e.g. *n*-alkyl or *n*-alkoxy groups) to a polymer with a rigid backbone is a common and important strategy for generating solubility in organic solvents. In addition, the introduction of polar groups or ionic sites can allow dissolution in hydrophilic solvents and in water. Thus, by a consideration of these factors and logical synthetic manipulations of polymer structures, the dissolution of virtually all uncrosslinked polymeric materials can, in fact, be achieved. It should also be noted, however, that dissolution of polymers in solvents can still be slow for kinetic reasons, even when the process is thermodynamically favorable. When a solid sample of a polymer dissolves, permeation of solvent into the solid from the solid/solvent interface can be slow, as long polymer chains must be completely solvated before diffusion into the bulk solvent is possible. Such a process is generally much more rapid for molecular compounds with smaller dimensions. Finally, it

should be noted that crosslinked polymers swell but do not dissolve in solvents which otherwise dissolve the analogous uncrosslinked material. The degree of swelling is inversely dependent on the degree of crosslinking. This generates gels, which have a wide variety of uses. For example, hydrogels made from crosslinked hydrophilic polymers are used as contact lenses.

1.2.5
Block Copolymers

The polymers discussed in the previous section are derived from a single monomer, and are termed *homopolymers*. Physical mixtures of two or more polymers are termed *blends*, and these hybrid materials have useful combinations of properties derived from the constituent homopolymers. Generally, for reasons analogous to those leading to a low entropy of dissolution in solvents (Sect. 1.2.4), and in dramatic contrast to the situation for small molecule compounds, the entropy of mixing of two homopolymers ΔS_{mix} is very small. As this is usually insufficient to overcome the unfavourable and positive value of the enthalpy of mixing ΔH_{mix} the material will phase-separate into regions of immiscible homopolymers at the microscopic level [39]. It is difficult to overemphasize the tendency of two polymers to phase-separate even if the difference in chemical structure is small. For example, even high molecular weight polyethylene and deuterated polyethylene are not miscible in all proportions!

Copolymers contain repeat units derived from different monomers chemically bound in the main chain. Considering two different monomers A and B, it is possible to envisage random copolymer structures (e.g. …ABBABAABA…), alternating structures (…ABABAB…), and many others such as graft structures, where, for example, side chains formed from B are attached to a main chain derived from A. *Block copolymers* (…AAAAAABBBBBB…, or A-*b*-B) are a particularly interesting example of a copolymer architecture and these materials possess a range of remarkable and useful properties [45]. For example, diblock copolymers form colloidal dispersions in solvents that are selective for one of the blocks, where supramolecular micellar aggregates are formed, with the insoluble block forming the *core* and the soluble block forming the *corona* [45, 46]. These micelles are generally much more stable than those formed by small molecule surfactants and are usually spherical in nature (Fig. 1.6), although a range of remarkable architectures including cylinders, vesicles, and even onion-like structures have now been generated [47–49].

Micellar structures can be visualized after solvent evaporation by techniques such as transmission electron microscopy (TEM) or atomic force microscopy (AFM). The micellar aggregates can be studied in solution by static and dynamic light-scattering, which can give micelle sizes and aggregation numbers as well as information on the shape of the micelles formed. Crosslinking of either the core or corona has been studied as a means of making the micellar structures permanent in the sense that they do not dissociate into individual block copolymer molecules in the presence of a good solvent for both blocks [50–55].

In the solid state, phase-separation of immiscible blocks generally occurs to give nanodomains that can be ordered. For example, the diblock copolymer polysty-

dissolution in
block-selective solvent

corona

core
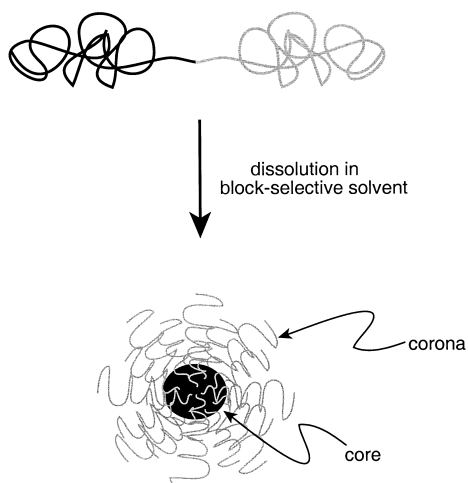
Fig. 1.6 Formation of spherical micelles from a block copolymer in a block-selective solvent.

0.00	0.17	0.28	0.34	0.62	0.66	0.77	1.00
PS spheres	PS cylinders	PS OBDD	PS, PI lamellae	PI OBDD	PI cylinders	PI spheres	

increasing volume fraction of PS ⟶

Fig. 1.7 Polystyrene-*b*-polyisoprene (PS-*b*-PI) solid-state morphologies as a function of increasing volume fraction of the polystyrene block (Adapted from [56]).

rene-*b*-polyisoprene (PS-*b*-PI) has been particularly well-studied, and ordered arrays of spheres, cylinders, bicontinuous double-diamonds (OBDD), and lamellae are formed as the relative block lengths (and hence block volume fractions) are altered from highly asymmetric through t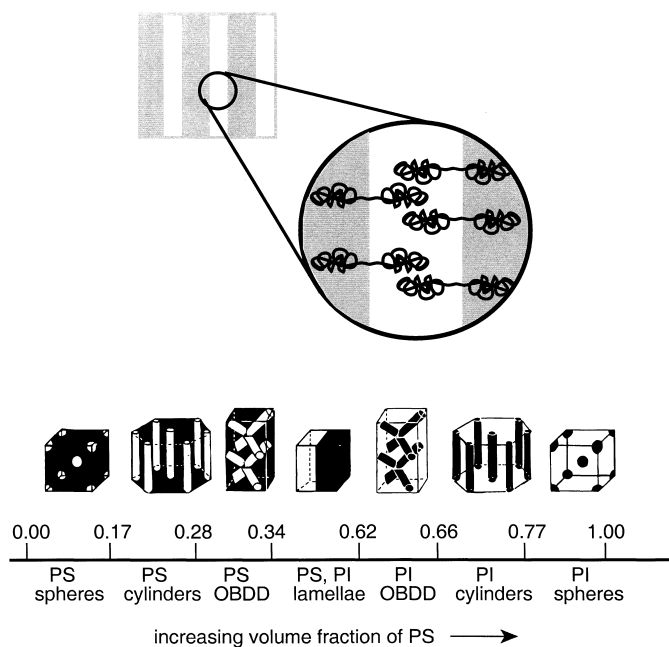o a similar value (Fig. 1.7) [45, 56]. More complex structures, such as gyroids, are formed within a relatively restricted range of block lengths. The structures can be imaged by techniques such as TEM and AFM, and further information on the order present in such systems can be revealed by techniques such as SAXS [43, 56].

The micellar structures and phase-separated domains have dimensions on the nanometer scale and are of considerable interest for a wide range of applications. These include uses as micellar drug delivery agents and catalysts, as nanoscopic etching resists for creating patterned surfaces in nanolithography, and for the generation of structures with periodic changes in refractive index for applications in photonics [45, 46, 57–61].

An elegant example that illustrates the enormous potential of this area is that provided by the use of the hydrophilic polyether domains of phase-separated polyisoprene-*b*-poly(ethylene oxide) (PI-*b*-PEO) as a reaction medium for the sol-gel hydrolysis of silicon and aluminum alkoxides [62]. The resulting structures can, for example, be subsequently dispersed in a solvent and consist of crosslinked silica/alumina/PEO nano-objects solubilized by the polyisoprene chains (Fig. 1.8).
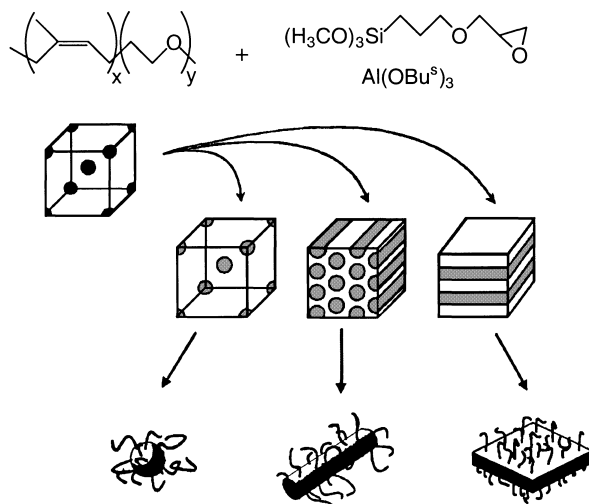
Fig. 1.8 Nano-objects with controlled shape and size from block copolymer mesophases: At the top left, phase-separated PI-*b*-PEO is shown, where the spheres consist of the PEO block. Subsequent dispersion and sol-gel hydrolysis of silicon and aluminum alkoxides in the PEO block leads to swelling of this block and, if desired, morphological transitions. Dissolution of the PI block in a selective solvent leads to "hairy" nano-objects consisting of crosslinked silica/alumina/PEO (Adapted from [62]).

Important commercial uses of block copolymers depend on phase separation in the solid state. For example, triblock copolymers PS-*b*-PB-*b*-PS (PB = polybutadiene) that contain a long PB block form glassy domains of PS (T_g=100 °C) within a matrix of low T_g PB ($T_g \approx$ –100 °C). The glassy PS domains function as physical crosslinks, which prevent the PB chains from slipping past one another under deformation. This generates elastomeric properties but, unlike normal elastomers which are permanently chemically crosslinked, heating above the T_g of the PS block allows the material to be reprocessed. This reversibility has led to the term *thermoplastic elastomer* for these materials, which are known as Kratons and are sold commercially [39].

1.2.6
Dendrimers and Hyperbranched Polymers

The area of tree-like polymer architectures was pioneered by the Tomalia, Newkome, and Vögtle groups in the late 1970s and 1980s [63–66]. The original syntheses of dendritic structures involved a *divergent* approach, where the structures were assembled by starting at a core and working outwards. Additional impetus to the area was subsequently provided by the demonstration of a new conceptual approach to dendrimers, which involved *convergent* synthesis, as reported almost simultaneously by the groups of Neenan and Miller, and by Hawker and Fréchet in 1990 [67, 68]. Here, the dendrimer was synthetically assembled by the reaction of a series of arms at a core. These two different methods are illustrated in Fig. 1.9.

The general area of dendritic and hyperbranched polymers has received remarkable attention over the past decade. New properties not available with linear polymers have been demonstrated. For example, evidence has been provided that supports the existence of considerable space for the encapsulation of small molecules, and this has led to the idea of a "dendritic box" [69]. A severe problem with dendrimers is their time-consuming synthesis and, recently, facile synthetic methods that form hyperbranched materials that may exhibit many of the advantageous properties of dendritic macromolecules have been receiving significant attention [70].

1.2.7
Electrically Conducting Polymers

Most polymers (typified by polystyrene and polyethylene) are electrically insulating and have conductivities $\sigma < 10^{-14}$ S cm^{-1}. The observation that polyacetylene could be oxidatively doped with iodine to become electrically conducting (values have now been reported up to $\sigma > 10^5$ S cm^{-1}) represented a pivotal discovery in polymer science that ultimately resulted in the award of the Nobel Prize for Chemistry in 2000 [4]. The study of electrically conducting polymers is now well advanced and two extremes in the continuum of transport mechanisms exist. If the charge carriers are present in delocalized orbitals that form a band structure along the polymer backbone, they conduct by a *delocalization* mechanism. In contrast, isolated groups in a polymer can function as acceptors or donors of electrons and can permit

a)

b)
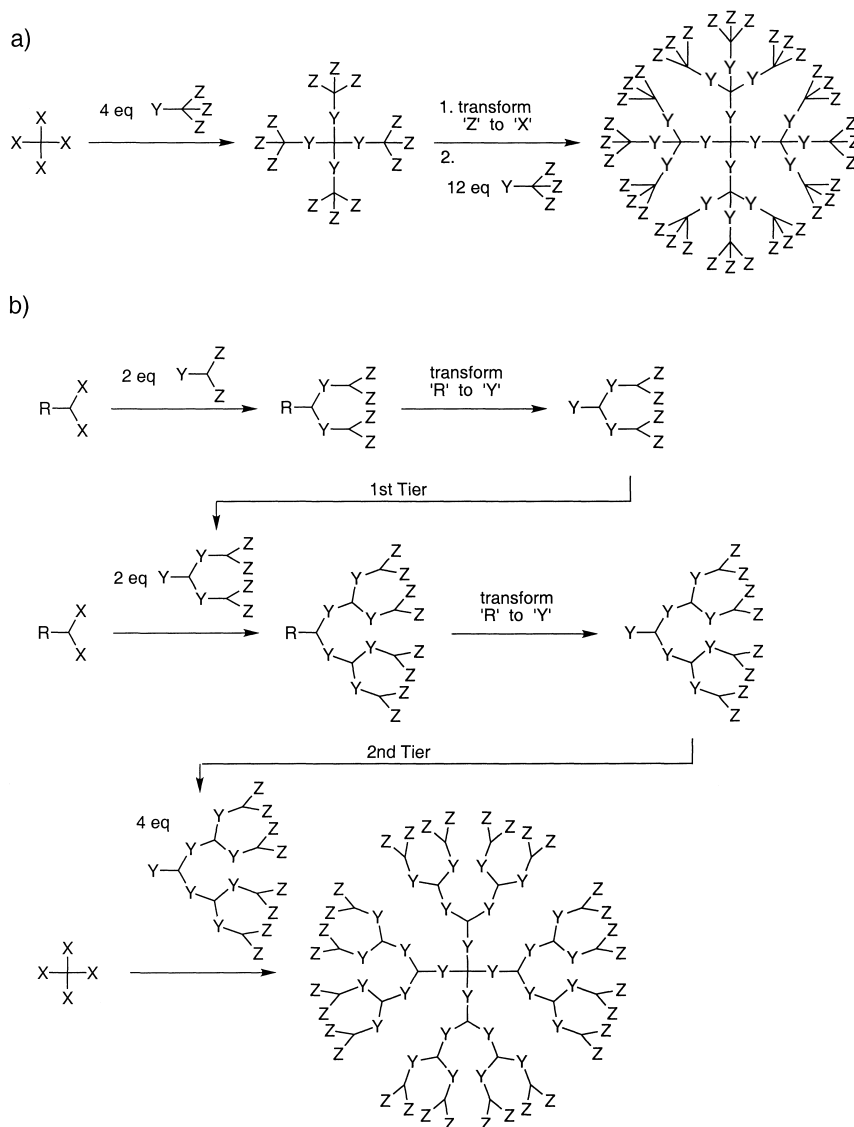
Fig. 1.9 Syntheses of dendrimers: (**a**) Divergent method, (**b**) convergent method.

charge transport of electrons or holes by a *redox conduction* or *hopping* mechanism. Although the conductivities observed in the former case are generally appreciably higher, both types of system are of considerable interest depending upon the conductivity desired for a particular application. High conductivities are desirable for many device applications, and materials such as polythiophene (**1.15**), polyaniline (**1.16**), and polypyrrole (**1.17**) have attracted much attention [6, 71]. On the other

hand, the semiconductivity of poly(vinyl carbazole) (**1.18**) ($10^{-7} < \sigma < 10^{-5}$ cm^{-1}) has led to interest in its use as a hole-transport material in xerography.
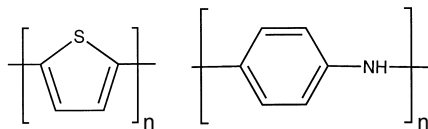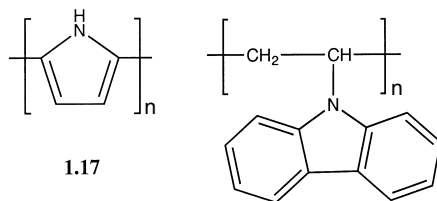
It should be noted that, in addition to their use as electronic conductors, polymers can also function as ionic conductors. Materials such as poly(ethylene oxide) and certain oligoethyleneoxy-substituted polyphosphazenes and polysiloxanes, which conduct Li$^+$ ions, are used in this regard as polymeric electrolytes for battery applications [9].

## 1.3
Motivations for the Incorporation of Metals into Polymer Structures

As mentioned earlier (Sect. 1.1), transition metal complexes and metal-containing solid-state materials are well-studied, and the presence of metal centers has been shown to give rise to a diverse range of interesting and often useful redox, magnetic, optical, electrical, and catalytic properties. In addition, metal centers have been shown to play a pivotal role with respect to both the structure and function of many biopolymers such as metalloproteins. The incorporation of transition metals into the structure of synthetic polymers, therefore, clearly offers considerable potential for the preparation of processable materials with properties that differ significantly from those of conventional organic polymers. For this reason, the development of metal-containing polymers should create exciting new dimensions for polymer materials science and, from an applied angle, significant applications for some of these unique new materials are also to be expected.

Several different possible types of metal-containing polymer structures exist, depending on where the metal atoms are incorporated and the nature of the linkages between them. A major subdivision of linear polymers involves a considera-

I (side chain)

II (main chain)

Ⓜ = metallo-group

〰 = spacer

III (dendritic/hyperbranched)
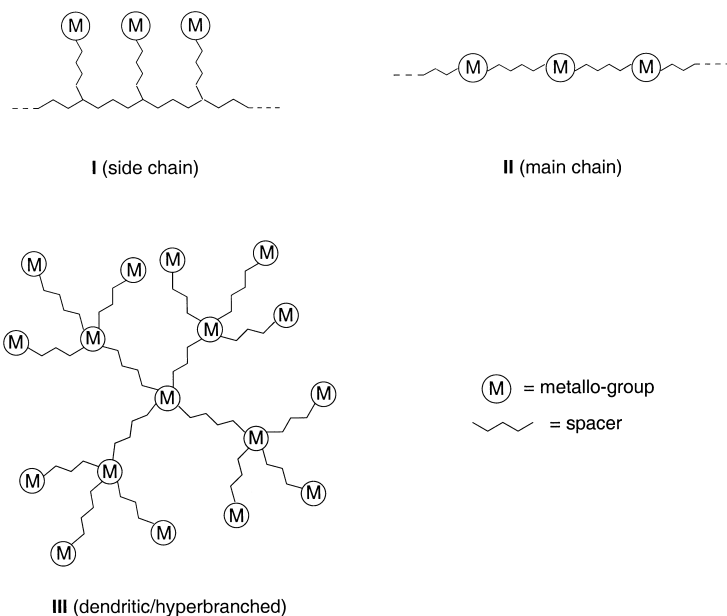
Fig. 1.10 Structural classes of metal-containing polymers.

tion of the location of the metallo-centers. These can be either in the side-group structure (**I**) or directly in the main chain (**II**) (see Fig. 1.10). We will use this general subdivision, although we note that these situations represent extremes. For example, a situation that lies in between these two cases is one in which the metal-containing moiety can be removed from, but is electronically coupled to, the polymer backbone. In addition, it is possible to prepare materials with metals in both the side-group structure and the main chain. Dendrimers and hyperbranched polymers (**III**) (Fig. 1.10) represent another structural class of growing interest. In this case, the metallo-centers can be located throughout the structure or, alternatively, in the core or at the periphery.

The linkages or "spacers" between the metallo-centers can either possess conjugated structures (involving delocalization of σ- or π-electrons) or essentially localized electrons. Again, these situations represent extremes, and partial conjugation is often possible. Studies of how the electronic structure of the linker can be changed to control interactions between the metals is an important area of research and has important implications for the physical properties (e.g. conductivity, magnetic properties) and applications of the materials.

It is useful to consider the types of characteristics expected for metal-containing polymers that provide a key motivation for making the materials. Some of the main reasons for the incorporation of metals into polymer structures are now outlined.
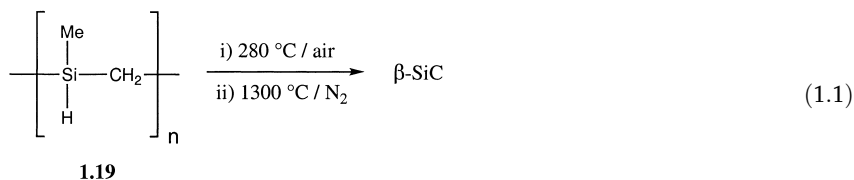
1.3.1
Conformational, Mechanical, and Morphological Characteristics

A carbon atom is small and is usually limited to coordination numbers ≤4, and is generally restricted to three geometries – linear, trigonal planar, and tetrahedral. The properties of organic polymers depend acutely on the nature of the polymer chain and the side groups. By contrast, metal atoms cover an enormous range of sizes and can exhibit a broad array of coordination numbers; values of up to 12 are well known and of up to 8 are common [72]. In addition, a wealth of geometries is known for metal centers. For example, in contrast to carbon, four-coordinate metal complexes can possess either tetrahedral or square-planar geometries. The flexible bonding characteristics of transition metals can also give rise to structures that are completely unprecedented in carbon chemistry. For example, metal-metal quadruple bonds are well-known, and metallocenes and cyclobutadiene complexes exhibit a totally different type of geometry to that found in organic molecules. In ferrocene, the prototypical metallocene, rotation about the iron-cyclopentadienyl bond is virtually unhindered. It is interesting to think about the influence that these novel structural features might have on the conformational, mechanical, and morphological properties of a polymer. Bearing in mind the immense structural diversity possible with metal complexes, this would clearly be expected to be a fascinating area. In addition, the diverse range of coordination numbers and geometries available for transition elements offers the possibility of accessing interesting liquid-crystalline materials [36].

1.3.2
Precursors to Ceramics

The possibility of using polymers, which can be easily processed into shapes, films or fibers, as precursors to ceramics has attracted intense recent interest [73–78]. Ceramics generally possess many desirable physical properties, such as hardness and useful electronic or magnetic properties, but their processability is generally poor. Polycarbosilanes have been successfully used to prepare silicon carbide monoliths and fibers by a pyrolysis technique, and a similar process that utilizes polyacrylonitrile has been used to make carbon fibers. For example, polycarbosilane **1.19** (Eq. 1.1) can be spun into fibers, which can then be heated in air to create a coating of SiO_2 that prevents melting. Subsequent thermal treatment at $800\,°C$ yields amorphous SiC fibers, and at higher temperatures these are increasingly reinforced and strengthened by the presence of β-SiC crystallites [77]. The key to the success of this process is to use a polymer that, when pyrolyzed, forms the desired ceramic product in high yield, and allows the shape of the precursor polymer to be retained.

$$\left[\begin{array}{c} \text{Me} \\ | \\ -\text{Si}-\text{CH}_2- \\ | \\ \text{H} \end{array} \right]_n \xrightarrow[\text{ii) 1300 °C / N}_2]{\text{i) 280 °C / air}} \quad \beta\text{-SiC} \qquad (1.1)$$

1.19

Transition metal-based polymers might also be expected to function as convenient precursors to metal-containing ceramic films, fibers, and coatings that would have high stability, and desirable/useful electronic or magnetic properties following thermal or photochemical treatment or exposure to ionizing radiation or plasmas. This provides a further motivation for making and studying metal-containing polymeric materials.

1.3.3
Magnetic, Redox, Electronic, and Optical Properties

Carbon atoms strongly prefer a spin-paired, singlet ground state and, as a consequence, the vast majority of organic compounds are diamagnetic. In contrast, transition metals routinely form stable ions in which unpaired electrons are present. Indeed, the existence of cooperative interactions, which allow the alignment of the magnetic moments of transition metal ions in the solid state, forms the basis of the vast array of magnetic materials in applications from computer discs to video tapes. The possibility of accessing polymers that possess magnetic moment alignment, and consequently ferromagnetic, ferrimagnetic, or superparamagnetic properties in the solid state, provides an additional reason for interest in metal-based polymers [36, 79]. Clearly, processable materials of this type would be of considerable interest for many applications. However, the design would have to be intricate. In addition to the presence of cooperative interactions along a linear polymer chain, 3-D cooperative intermolecular interactions between the chains would also need to be present. In the absence of an ordering mechanism, the materials would be paramagnetic and of less interest. Moreover, if the alignment were antiparallel, even less useful antiferromagnetic materials would result [36].

As a consequence of their electronic structure, metal atoms (especially those of transition elements) generally exist in a variety of oxidation states. This can be expected to facilitate access to redox-active materials. In addition, the low electronegativity of transition metal atoms should promote electron mobility and access to interesting charge-transport properties. This is apparent when a metalloid such as silicon or germanium is used to form polymer chains. Thus, whereas polyethylene possesses an essentially localized backbone, polysilanes (**1.3**) and polygermanes (**1.20**) possess σ-delocalized electronic structures, and doping with oxidants allows semiconducting materials ($\sigma > 10^{-5}$ S cm^{-1}) to be obtained, in which holes are the charge carriers [9]. Such unusual characteristics are expected to be further enhanced if even more electropositive metallic elements are used to construct polymer chains. The presence of transition metal centers can also impart interest-

ing photophysical properties [80]. Due to spin-orbit coupling effects, long-lived triplet excited states are often readily accessible and phosphorescence is a well-established and useful phenomenon. Photoinduced charge transfer processes have been well-studied and form the basis for many explorations of the photocatalytic properties of transition metal complexes. Areas such as nonlinear optics and photonics, which require access to processable materials with electron delocalization and polarizability or high refractive indices, may also benefit from the incorporation of metals into polymer structures [80].

$$\left[\begin{array}{c} R \\ | \\ -Ge- \\ | \\ R \end{array} \right]_n$$
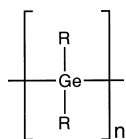
1.20

1.3.4
Catalysis and Bioactivity

The ability of transition metals to bind and activate organic molecules, and to release the transformed organic product with turnover, forms the basis of the vast catalytic chemistry of transition metal complexes [81]. In addition, metal atoms play a key role at the catalytic centers of many enzymes [82]. For example, metalloenzymes participate in hydrolysis, oxidation, reduction, electron-transfer chemistry, and many other remarkable processes such as nitrogen fixation. The long-term development of synthetic polymers that perform catalytic chemistry in a manner analogous to enzymes is a goal of profound interest. The use of a polymer would facilitate product separation and catalyst recycling, particularly if the material were crosslinked and therefore insoluble in the reaction medium. To date, most work has focused on the use of an organic polymer backbone with catalytically active metals bound to ligands in the side-group structure. Problems with this approach have arisen due to leaching of the catalytically active transition metal from the polymer. In addition, in contrast to the situation with enzymes, relatively low activities have often been reported due to the difficulty associated with substrates accessing the catalytic centers. However, recent results have appeared much more promising and improvements in polymer design and synthetic control over the polymer structure offer hope that these deficiencies will be overcome in the future.

Many metal complexes have been shown to possess bioactivity and several drugs based on metal complexes have been developed. These include platinum, gold, and bismuth compounds used in the treatment of certain kinds of cancer, arthritis, and stomach ailments, respectively [82]. The development of analogous polymeric chemotherapeutic materials, that would less easily diffuse through membranes, is also an important objective.

1.3.5

Supramolecular Chemistry and the Development of Hierarchical Structures

Studies of biological systems have revealed that functional structures in Nature generally display hierarchical order in that they are organized over a variety of length scales [46, 82]. For example, hemoglobin, the oxygen-transporting metalloprotein in blood, is a superstructure made up of four subunits, two α- and two β-polypeptide chains, each with an oxygen-binding iron porphyrin group [82]. The overall superstructure, which is illustrated for the carbon monoxide complex carboxyhemoglobin, in which CO is coordinated to iron (Fig. 1.11), can be analyzed in terms of quaternary, tertiary, secondary, and primary structures, which together provide the optimal functioning of the material [83].

A challenge of considerable interest for the future is to learn how to apply self-assembly principles that involve the use of non-covalent interactions, to the generation of new synthetic materials with hierarchical order [46]. To take an illustrative, previously discussed example, monomer molecules can be converted into block copolymer macromolecules (Sect. 1.2.5). These subsequently self-assemble into structures with higher degrees of order, as illustrated by the formation of the various morphologies of phase-separated block copolymers in the solid state (Fig. 1.7) [45, 56]. Exciting general progress is now being made in the synthesis of hierarchical structures. An elegant example is provided by the use of hydrogen-bonding and van der Waals interactions to assemble individual flat poly(benzyl ether) dendrimer arms or "dendrons" into cylindrical columnar assemblies that self-organize into a 2-D hexagonal lattice (Fig. 1.12) [84].
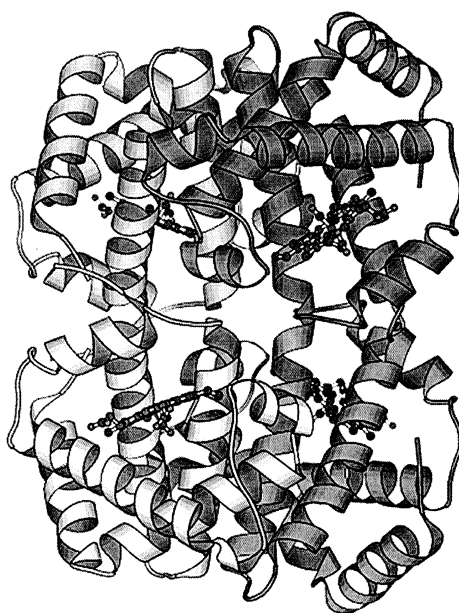
Fig. 1.11 The structure of carboxyhemoglobin (Reproduced from [83]). 4 iron porphyrin centers are present.
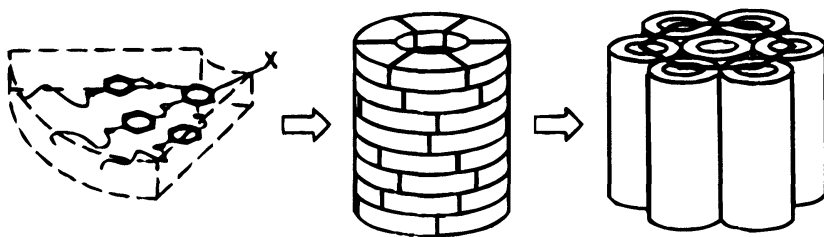
Fig. 1.12 Hierarchical self-assembly of flat monodendrons into cylindrical columnar assemblies that self-organize into a 2-D hexagonal lattice (Reproduced from [84]).

Significantly, the incorporation of transition elements into self-organizing motifs provides additional possibilities for supramolecular chemistry and the properties of the resulting assemblies. For example, as mentioned above, the coordination numbers and geometries accessible with transition metals vary much more widely than with carbon. Applications in the area of liquid-crystalline materials are particularly promising, as an almost unlimited diversity of structure appears possible with metallomesogens [36]. In addition, metallic elements provide new types of "weak" interaction that supplement the well-known hydrogen bonds, which play such a key role in the determination of the 3-D conformational structures of biopolymers such as nucleic acids. For example, unconventional hydrogen (or "hydride-proton") bonds ($H^{\delta-}\cdots H^{\delta+}$) involving electron-rich (e.g. metal hydride) and electron-poor hydrogen substituents have been used to generate novel materials with extended structures in the solid state [85]. Interactions between gold atoms ($Au\cdots Au$) or "aurophilic bonds" have approximately the same strength as conventional hydrogen bonds, and are a consequence of the relativistic effects that are significant for heavy metal elements. These have also been used to facilitate the formation of remarkable chain and catenane structures [86–88]. In addition, weak coordination bonds between vanadyl groups ($V=O\cdots V=O$) have been used to generate liquid-crystalline ordering [89]. The exploitation of such interactions at the polymer level, and the development of metallopolymers (e.g. block copolymers) that undergo self-assembly to form metal-containing structures that are ordered on the nanometer scale, is of intense interest. The creation of new types of supramolecular functional materials with a wealth of attractive properties and potential applications that complement those accessible with organic materials is a logical consequence [90].

1.4
Historical Development of Metal-Based Polymer Science

It is both interesting and informative to briefly consider the historical development of the metal-containing polymer field. Without attempting to be exhaustive, a selection of some of the key breakthroughs, with an important influence on the development of the area (see Fig. 1.13), are discussed below.
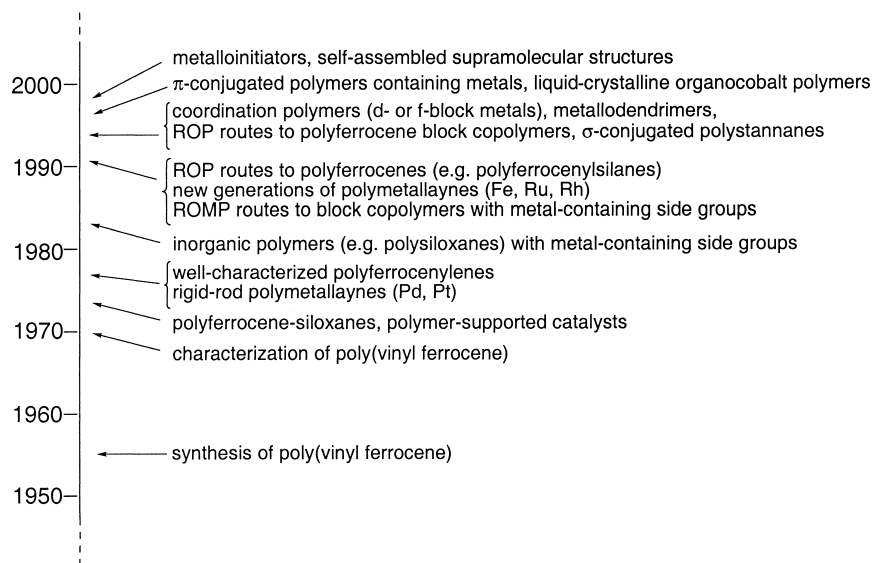
2000— metalloinitiators, self-assembled supramolecular structures
π-conjugated polymers containing metals, liquid-crystalline organocobalt polymers
coordination polymers (d- or f-block metals), metallodendrimers,
ROP routes to polyferrocene block copolymers, σ-conjugated polystannanes

1990— ROP routes to polyferrocenes (e.g. polyferrocenylsilanes)
new generations of polymetallaynes (Fe, Ru, Rh)
ROMP routes to block copolymers with metal-containing side groups

1980— inorganic polymers (e.g. polysiloxanes) with metal-containing side groups
well-characterized polyferrocenylenes
rigid-rod polymetallaynes (Pd, Pt)

1970— polyferrocene-siloxanes, polymer-supported catalysts
characterization of poly(vinyl ferrocene)

1960—

synthesis of poly(vinyl ferrocene)

1950—

Fig. 1.13 Some key breakthroughs in the field of metal-containing macromolecules.

The birth of polymer science can be traced to the acceptance of Staudinger's hypothesis, that polymeric materials are comprised of long chain macromolecules, in the early 1930s. This led to the rapid subsequent synthetic development of organic polymers and parallel studies of their physical properties. The first soluble metal-containing polymer, poly(vinyl ferrocene) (**1.21**), was prepared by radical polymerization in 1955. With the growing interest in new polymeric materials with novel properties, the 1960s and early 1970s was a time of much activity in the area of metal-containing polymer science. However, few, if any, well-characterized, soluble, high molecular weight materials were actually reported during this period. The first well-characterized polymer of appreciable molecular weight with metal atoms in the main chain, a polyferrocene-siloxane material (**1.22**), was prepared by Pittmann in 1974 by a polycondensation strategy. Noteworthy work by Neuse later in the same decade led to well-characterized but rather low molecular weight polyferrocenylenes (**1.23**). Also in the late 1970s, the first reports of members of the important class of rigid-rod polymetallayne polymers containing Pd and Pt (**1.24**) were made by Hagihara, Takahashi, and Sonogashira [91].

1.21   **1.22**
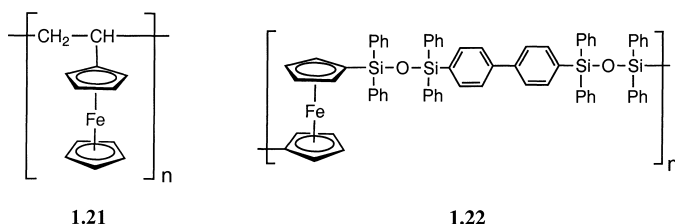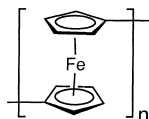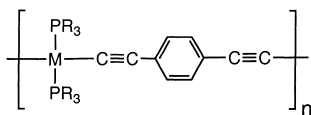
1.23   **1.24** M = Pd or Pt

A series of important developments in the area of metal-containing polymers occurred in the 1990s as a consequence of a range of key synthetic break-throughs. For example, ROP routes and ROP-related processes have provided access to polymetallocenes such as polyferrocenylsilanes (**1.25**) and analogues with, for example, disulfido spacers (**1.26**). Also included are main-chain metal-containing polymeric materials with controlled architectures, such as block copolymers [90, 91]. In the early 1990s, homopolymers and block copolymers with metal-containing side groups were also made available by the technique of ring-opening metathesis polymerization (ROMP) [92]. In 1993, transition metal-catalyzed poly-condensation strategies yielded the first polystannanes (**1.27**), with main chains consisting of tin atoms, and well-defined organocobalt polymers and coordination polymers (e.g. **1.28**) incorporating a variety of transition metal elements or lanthanide metals were described [90, 91, 93]. Star and dendritic materials containing metal atoms either in the core, at the periphery, or distributed throughout the structure were also described around the same time [94, 95]. An exciting development from the late 1990s involves the creation of metallo-initiators for controlled polymerization reactions that have considerable synthetic potential [96]. An interesting feature of many of the polymers prepared in the late 1990s is the presence of metal atoms as an integral part of the main chains of heteroaromatic π-conjugated polymeric frameworks. These materials (e.g. **1.29**) are the focus of growing interest [97, 98]. Self-assembled and hierarchical structures based on metal-containing polymers, such as liquid crystals, self-assembled block copolymer micelles and superlattices, are also starting to attract intense attention, and this area is set to expand rapidly during the 21st century [90, 99–102].
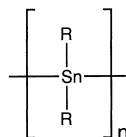
Full details of these contributions, together with many others of arguably comparable significance, can be found in the subsequent chapters. In the final section of this Introduction, the currently available range of synthetic routes for making polymers with metals in the side-group structure or main chain are reviewed.
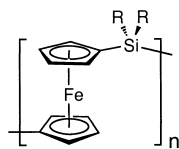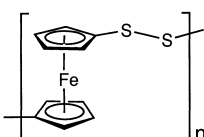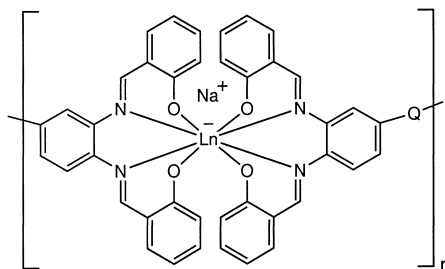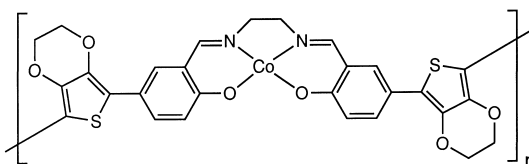
1.25   **1.26**   **1.27**

Ln = Eu, La, Gd, Y, Yb

Q = —, CH$_2$, SO$_2$

1.28

1.29

1.5
Synthetic Routes to Metal-Containing Polymers

1.5.1
The Synthesis of Side-Chain Metal-Containing Polymers

The incorporation of metallic elements into the side-group structure of high molecular weight organic and inorganic polymers has, in general, been well-developed. Such materials are generally accessible by subtle variations of the synthetic methods used to prepare the metal-free materials and can often take advantage of well-established organic functional group chemistry. Representative examples of typical syntheses include the free radical polymerization of vinylcymantrene to yield poly(vinylcymantrene) (**1.30**, Eq. 1.2) [103, 104], and the formation of polysilanes (**1.31**, Eq. 1.3) and polyphosphazenes (**1.32**, Eq. 1.4) with metallocene side groups, by condensation and ring-opening polymerization, respectively [105, 106]. The attachment of organometallic moieties to phosphinated polystyrene (to give **1.33**, Eq. 1.5) and to poly(propyleneimine) dendrimers (to afford **1.34**, Eq. 1.6) provide further examples of successful synthetic strategies [107, 108].

$$(1.2)$$

1.30

$$(1.3)$$

1.31

$$(1.4)$$

1.32

$$(1.5)$$

1.33
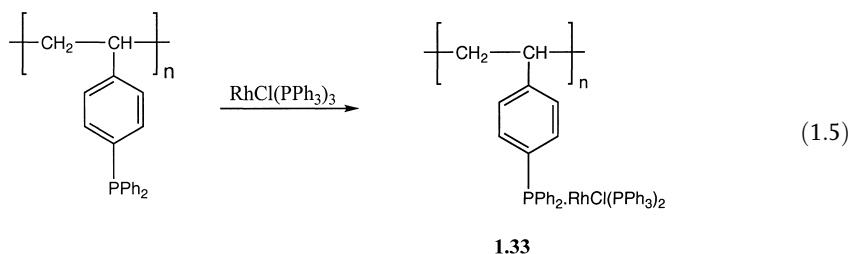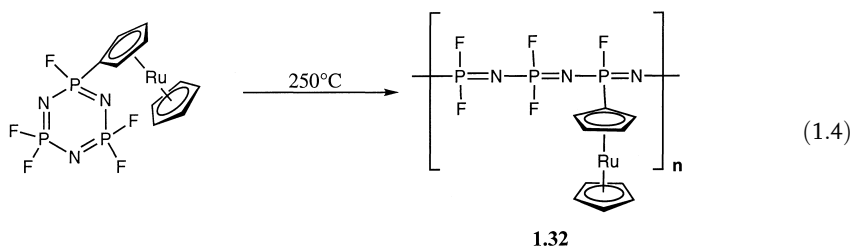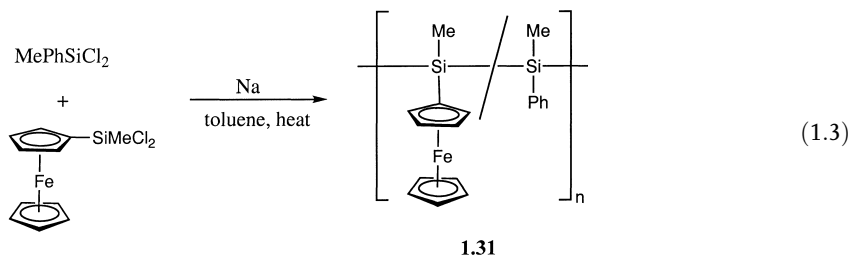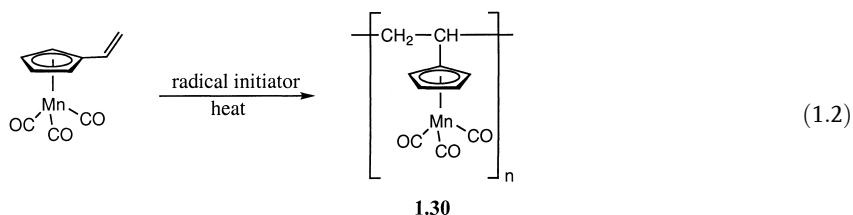
In certain cases, the presence of the metal-containing moiety can lead to significant restrictions upon the methods of polymerization that can be used. For example, in the case of polysilanes with ferrocene side groups (**1.31**) prepared by Wurtz coupling, it was found that attempts to introduce high loadings of ferrocene were unsuccessful and only relatively low loadings of the organometallic moiety were found to be achievable [105].

M = Fe, z = 0
+
M = Co, z = 1

$$(1.6)$$

1.34
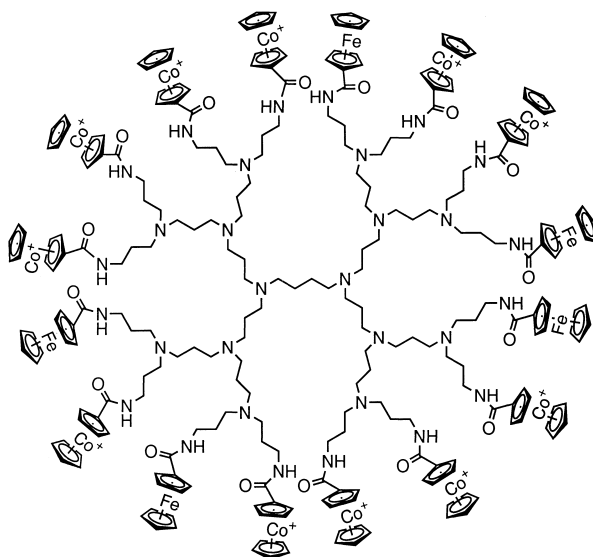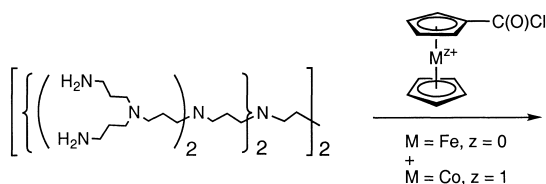
1.5.2
Main-Chain Metal-Containing Polymers

1.5.2.1 Why are Transition Metals in the Polymer Main Chain Desirable?

For many applications, side-chain metal-containing polymers are sufficient. However, to access the most profound alterations in polymer properties that arise from the presence of metal atoms in a polymer structure, incorporation in the main chain is required. Potential advantages of including metals in the backbone of a polymer rather than in the side-group structure include the following:

1. The influence of the varied geometries of transition metal centers on the conformational and thermophysical properties would be more significant.
2. The development of materials with properties that depend on the ability of the metal atoms to interact with one another in a controlled manner would be facilitated, as smaller changes in M $\cdots$ M distance accompany backbone motions compared to those of side groups.

3. Access to interesting charge-transport properties and other characteristics that depend on delocalization effects would be favored as the metal could potentially be placed directly in the conjugation pathway.

4. Leaching of the metal from the polymer would be expected to be less problematic and this might be significant for catalytic or preceramic applications.

Unfortunately, compared to side-chain metallopolymers, the synthesis of main-chain metal-containing polymers is much less developed, although significant progress has been made over the last two decades of the 20th century. In short, the construction of long chains containing metal atoms represents a challenging synthetic problem. Moreover, very significantly, the synthetic problem becomes ever more challenging as the distance between the metal atoms in the backbone of the prospective polymeric material decreases and, consequently, the degree of "metallization" becomes more substantial and the possibility for interesting metal-metal interactions is enhanced.

1.5.2.2 The Synthesis of Main-Chain Metal-Containing Polymers

Consideration of the main synthetic routes to organic polymers illustrates the problems associated with the synthesis of main-chain metal-containing polymers (see Scheme 1.1). There are two main methods of polymer synthesis – *chain-growth polymerizations* and *step-growth polymerizations* [7]. Chain-growth processes involve initiation, propagation and, usually, termination and chain-transfer steps. Very significantly, the presence of reactive intermediates (radicals, cations, anions, organometallic species, etc.) that react rapidly with monomer molecules in an efficient propagation step, generally allows the facile formation of high molecular weight polymeric materials. Indeed, a usual characteristic of this type of polymerization is that a high molecular weight polymer is formed even at low monomer conversion. In contrast, in step-growth polymerizations, the reaction intermediates are of comparable reactivity to the monomers, and the generation of high molecular weight materials requires stringently accurate reaction stoichiometry and ca. 100% monomer conversion [7].

1.5.2.2.1 Addition Polymerization

Addition polymerization of unsaturated organic molecules (*α*-alkenes, acetylenes, isonitriles, etc.) provides a versatile and industrially important route to many organic polymers. Such processes have as their thermodynamic driving force the conversion of π-bonds into new and more stable σ-bonds and proceed by a chain-growth mechanism that involves radicals, anions, cations or other reactive species as intermediates. However, analogous polymerizations are very difficult to use for the synthesis of metal-containing polymers, as suitably reactive but stable multiple bonds involving metallic elements are relatively difficult to prepare. In contrast to the situation for organic molecules, the isolation of stable species with multiple bonds that involve metallic elements usually requires the presence of sterically demanding, oligomerization-inhibiting ancillary ligation. Although the
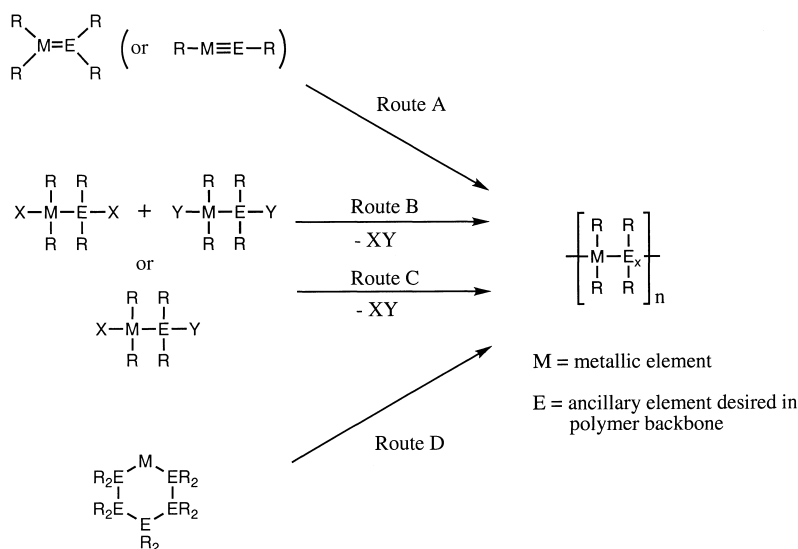
Scheme 1.1

addition polymerization of examples of these materials is of great potential interest (Scheme 1.1, Route A), such chemistry is virtually unexplored and very few studies have been reported. In the case of species such as $[Cl_3M \equiv N]_\infty$ (M = Mo or W), with metal-nitrogen multiple bonds, individual monomers (**1.35**) seem to be preferred, as attempted dissolution of solid-state materials (**1.36**) that contain extended M–N chains leads to depolymerization (Eq. 1.7). The structures of the latter materials have been analyzed by single-crystal X-ray diffraction and show the presence of alternating strong (effectively triple) and very weak (< single) bonds in the metal-containing chains [109, 110]. Similar features have been observed for analogous vanadium systems $[Cl_2L_2V \equiv N]_\infty (L_2 = \text{diimine})$ [111].

$$(1.7)$$

1.5.2.2.2 Polycondensations

Early attempts to prepare main-chain metal-containing polymers mainly focused on the use of step-growth polycondensation processes (Scheme 1.1, Route B). These routes work well for the synthesis of carbon-based polymers when difunctional organic monomers are used because the latter are generally easily accessible in a high degree of purity. This allows the stringent stoichiometry and conver-

sion requirements that need to be fulfilled for the formation of high molecular weight polymers by step-growth polycondensation reactions to be satisfied. This type of methodology also works reasonably well if the metal atoms desired in the polymer backbone are well-spaced. In such cases, organic functional group chemistry can be used to successfully couple the monomers, provided that the synthetic transformations are compatible with the stability of the metal center. However, severe problems arise when polymeric materials with main-chain metal atoms in close proximity are desired. In these cases, the functional group chemistry needed for efficient monomer coupling is poorly developed and difunctional metal-containing monomers (dilithiated species, for example) are often so reactive that they are difficult to prepare and purify. Thus, in many cases, exact reactant stoichiometries for polycondensation reactions cannot be achieved. This generally results in the formation of low molecular weight oligomeric products that are well below the critical entanglement molecular weight necessary for the formation of fabricated materials (e.g. free-standing films, fibers, etc.) with reasonable mechanical strengths (see Sect. 1.2.3).

To appreciate the requirements for accessing high molecular weight polymers by step-growth polycondensation reactions, a more detailed discussion is desirable. To access substantial molecular weights ($M_n >$ ca. 10,000) using a polycondensation of two difunctional monomers (Eq. 1.8), two stringent criteria need to be satisfied. First, exact reaction stoichiometries are required (i.e. the functional groups must be present in equal amounts) and second, high conversions are necessary (i.e. the extent of reaction must be virtually 100%).

$$X—M—X$$
$$+ \qquad \xrightarrow{\text{-2 XY}} \qquad \left[\!\!\!\begin{array}{c} \\ M—E \\ \\ \end{array}\!\!\!\right]_n \qquad\qquad (1.8)$$
$$Y—E—Y$$
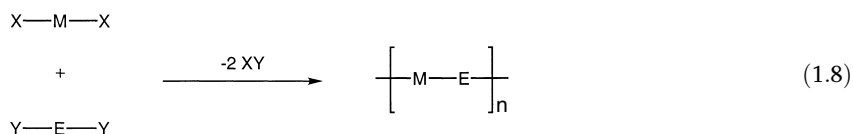
The dramatic influence that these two "stoichiometry" and "conversion" factors can have on molecular weight cannot be overemphasized, and can be explained in terms of the classic theory of polycondensation reactions developed by Carothers [7, 40]. Based on this theory, the *number average degree of polymerization DP_n* (i.e. the value of M_n divided by the molecular weight of a repeat unit) is given by the expression in Eq. 1.9.

$$DP_n = \frac{1+r}{1+r-2rp} \qquad\qquad (1.9)$$

DP_n = number average degree of polymerization
r = stoichiometric ratio of functional groups X and Y present
p = extent of reaction (the fraction of functional groups that have reacted)

Thus, high values of DP_n (i.e. high molecular weights) result when the stoichiometric ratio r and extent of reaction p have values close to unity. The "stoichiom-

etry" criterion is not normally a problem in organic polycondensation reactions as the difunctional monomers are usually easy to prepare and purify. However, the "conversion" criterion often presents a challenge and reactions must be driven to completion by, for example, the removal of a volatile small molecule product if high molecular weight polymers are to be generated. For metal-containing monomers the opposite is usually true. Reactions generally proceed to close to 100% completion (i.e., $p=1$) but, as mentioned above, difunctional, metal-containing (and, in general, inorganic) monomers are often highly reactive, and are therefore difficult to purify completely, or have poorly defined structures. This makes it very difficult to achieve values of the stoichiometric ratio r close to unity. This can be appreciated by a consideration of the limiting case of Eq. 1.9 when $p=1$ (Eq. 1.10).

$$\text{If} \quad p = 1 \qquad DP_n = \frac{(1 + r)}{(1 - r)} \tag{1.10}$$

The equation indicates that even if a reaction proceeds to 100% completion (i.e. if the conversion criterion is satisfied perfectly and $p=1$), the ratio of the pure difunctional monomers must still be 0.98 : 1.00 or better (i.e. $r > 0.98$) if values of M_n of 10,000 or greater are to be obtained. This calculation assumes that a monomer unit has a molecular weight of 100. Values of DP_n as a function of r for cases where $p=1$ are shown in Table 1.1 and illustrate the dramatic tail-off in DP_n and M_n as the stoichiometric ratio r deviates further from unity.

   Although the above considerations help to explain many of the failures to prepare high molecular weight metal-containing polymers by condensation routes in the 1960s and 1970s, highly efficient coupling procedures have been developed more recently, and these have contributed significantly to the renaissance of metal-based polymer science. An early example of the progress in this area is provided by the synthesis of rigid-rod organometallic polymers in the late 1970's; these fascinating polymers are discussed in detail in Chapter 5. Well-defined and efficient routes have also been used to prepare coordination polymers (e.g. **1.37**, Eq. 1.11). Metal-catalyzed coupling procedures of high efficiency have also been utilized to prepare polymers containing cyclobutadiene cobalt units (e.g. **1.38**, Eq. 1.12) [112, 113].

Table 1.1 Values of DP_n and M_n corresponding to different values of r in Eq. 1.10 for a hypothetical monomer of molecular weight 100

r	DP_n	M_n
1.00	∞	∞
0.99	199	19,900
0.98	99	9,900
0.97	66	6,600
0.96	49	4,900
0.95	39	3,900
0.90	19	1,900

$$[Cu(NCMe)_4][PF_6]$$

(1.11)

1.37

1.38

(1.12)
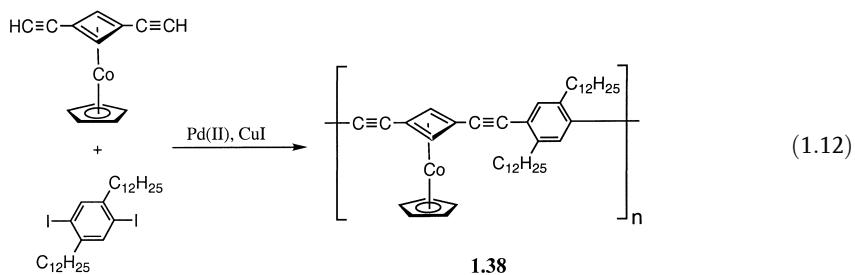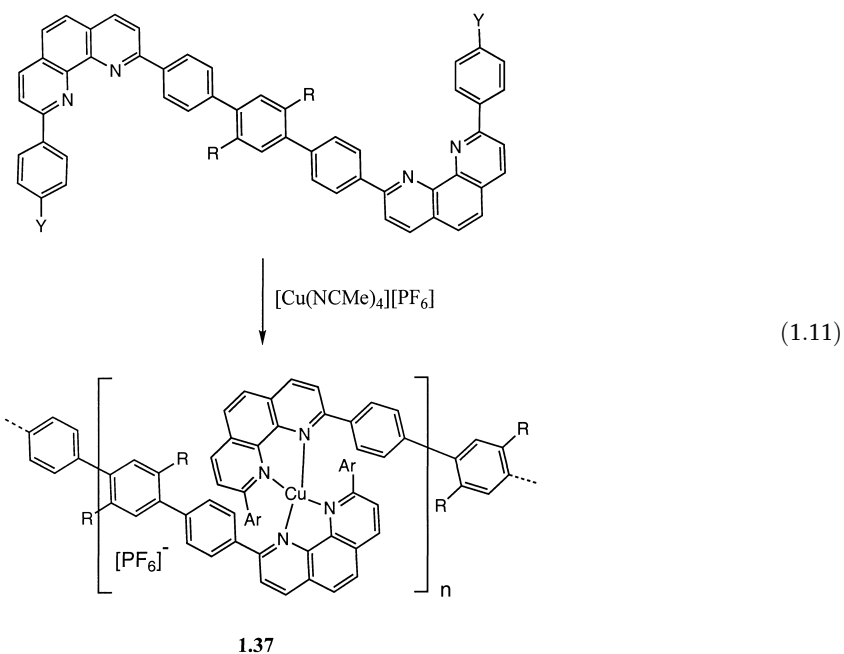
A very promising variant on this type of condensation polymerization involves the use of monomers that possess groups X and Y, which can be eliminated from the same molecule. This circumvents the need for careful control of reaction stoichiometry. Moreover, in certain cases, polymerization of monomers of this type can follow a chain-growth type of mechanism that leads to high molecular weights much more easily. Such processes (Scheme 1.1, Route C) have not yet been explored for the formation of metal-containing polymers, but are well-established for the synthesis of certain classes of polymers based on main-group elements such as polyphosphazenes (**1.2**) and polyoxothiazenes (**1.4**) [12, 16, 26].

1.5.2.2.3 **Ring-Opening Polymerization (ROP)**

A further common and important route to organic polymers involves ROP, and this methodology is used industrially to prepare nylon-6 and poly(ethylene oxide). In the vast majority of cases, the presence of ring strain provides the thermodynamic driving force for the ROP process [7]. Most examples of ROP proceed by a chain-growth route. Indeed, the discovery of ROP routes to polycarbonates and other materials has the advantage of providing access to polymers of more substantial molecular weights than those typically available by polycondensation [7].

Metal-containing rings are relatively well-known, but few have been studied with respect to their polymerization behavior. Nevertheless, in the last decade, a range of examples of successful ROP processes (Scheme 1.1, Route D) have been described for ferrocenophanes and related derivatives, and this has provided access to high molecular weight main-chain polymetallocenes. Thermal and transition metal-catalyzed ROP and metal-catalyzed ring-opening metathesis polymerization (ROMP) processes have been reported for metallocenophanes and yield ring-opened polymers (e.g. **1.39**, Eq. 1.13 and **1.40**, Eq. 1.14) [114, 115]. Several examples of living polymerizations have been achieved by the treatment of [1]ferrocenophanes with anionic initiators. No appreciable termination or chain transfer is observed and the resulting polymer chains have a very narrow molecular weight distribution ($M_w/M_n \approx 1$) [7]. The living nature of the ROP process allows the sequential polymerization of different monomers, and thereby provides access to block copolymers and other controlled architectures. For example, treatment of phosphorus-bridged [1]ferrocenophane **1.41** with BuLi yields the living anionic polymer **1.42**, which reacts with silicon-bridged [1]ferrocenophane **1.43** to yield the living block copolymer **1.44** and the polyferrocenylphosphine-*b*-polyferrocenylsilane block copolymer **1.45**, with a narrow polydispersity, upon hydrolytic work-up (Eq. 1.15) [116].

1.39

(1.13)

1.40

(1.14)

$$(1.15)$$
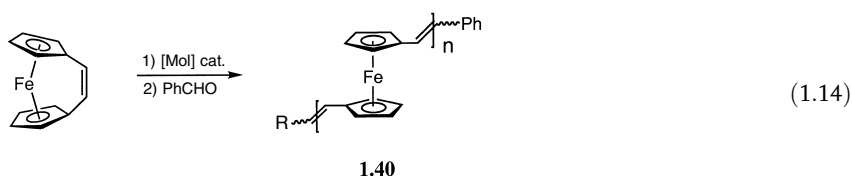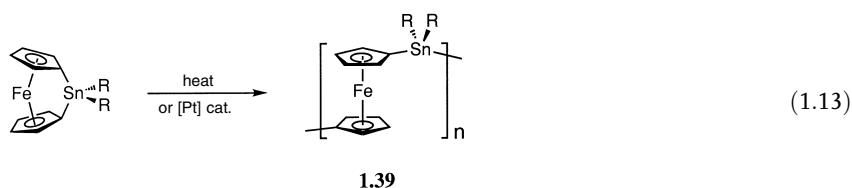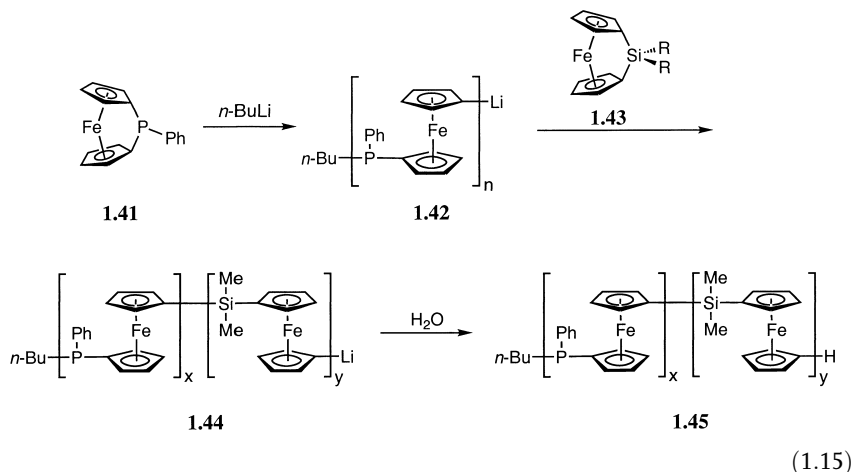
This survey of synthetic routes to metallopolymers completes the discussion of introductory topics in this chapter. In the following chapters, the main classes of metal-containing polymers will be discussed, with emphasis not only on synthetic details, but also on their properties and applications. The general philosophy will be to focus on well-characterized and well-studied materials which are truly polymeric in nature ($M_n > 10,000$, see section 1.2.3) rather than to exhaustively discuss every metallopolymer mentioned in the literature. Particular attention is given to examples where studies of properties and potential functions have been performed.

1.6
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