

Ian Manners

Synthetic Metal-Containing Polymers



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Synthetic Metal-Containing Polymers

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Cover Picture A depiction of the structure of metallated (Zn) DNA (see Chapter 7, section 7.6) superimposed on a polarizing optical micrograph that shows a lyotropic liquid crystalline mesophase formed by a Pt polyyne (see Chapter 5, section 5.2.3.2.)

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Preface

Polymer science has developed rapidly over the last few decades of the 20th century into an exciting area of high-tech materials research. A major contribution to this transformation has been provided by the infusion of creative ideas from synthetic organic chemists. Until recently, the impact of inorganic chemistry on polymer science has been much more limited in scope and has been primarily restricted to the discovery of highly active olefin polymerization catalysts. This is mainly a result of the challenging synthetic problems concerning the formation of long polymer chains containing elements other than carbon. These hurdles are now being overcome and the tantalizing possibility of exploiting the rich diversity of structures, properties, and function provided by inorganic elements in the development of new macromolecular and supramolecular polymeric materials is being productively realized. The new hybrid materials being created represent a welcome addition to the materials science toolbox, and impressively complement those now accessible using organic chemistry.

This book focuses on the area of metal-containing polymers which, based on the unique properties of transition elements and main group metals, exhibit particular promise. The work is organized to provide interested researchers in Universities and Industry with a critical review of the state of the art, and to help stimulate fundamental and applied research in the future. An overview of key concepts in polymer science and background to the challenges and motivations for the development of metal-containing polymers is provided in the introductory Chapter 1. Chapters 2–8 cover the different structural types of metallopolymer currently available with an emphasis on well-characterized materials, properties, and applications. Chapter 2 focuses on polymers with metals in the side group structure. Chapters 3–7 discuss the various classes of metallopolymer with transition or main group metals in the main chain. Dendritic and hyperbranched metallopolymer are described in Chapter 8. The structural diversity of the materials now available is impressive, as is the range of function. The extensive list of uses includes applications as catalysts, electrode mediators, sensors, and as stimuli responsive gels; as photonic, conductive, photoconductive, and luminescent materials; as precursors to magnetic ceramics and nanopatterned surfaces; and as bioactive materials and metalloenzyme models.

The creation of this book has been accomplished with the help of many other individuals. I would like to express my deep appreciation to a number of my grad-

uate students and postdocs who generously volunteered their talents and help with various aspects of this work. I would like to thank in particular Sara C. Bourke who provided exceptional help and valuable critique throughout the various stages of putting the manuscript together. I also wish to acknowledge the efforts of Katie Porter, Dr. Paul Cyr, Alex Bartole-Scott, Dr. Zhuo Wang, Dr. Xiaosong Wang, Sebastien Fournier, Keith Huynh and Fabio di Lena who helped with the correction and proof-reading of the various chapters. I would also like to thank my wife Deborah O'Hanlon-Manners for helpful comments, proof-reading, and very useful advice.

Finally, I would like to dedicate this book to the people from my personal life whose encouragement over the years has always been essential – my wife Deborah and children Hayley and Chris, my mother Jean D. Manners and late father Derek S. Manners, and my late grandmother Daisy M. Manners.

Ian Manners

Toronto, November 2003

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Abbreviations

A- <i>b</i> -B	diblock copolymer
A- <i>r</i> -B	random copolymer
Ac	acetyl group
ADIMET	acyclic diyne metathesis
ADMET	acyclic diene metathesis
AFM	atomic force microscopy
AIBN	azobisisobutyronitrile
Ar	aryl group
bipy or bpy	2,2'-bipyridine
cod	cyclooctadiene
Cp	cyclopentadienyl
DCC	dicyclohexylcarbodiimide
depe	bis(diethylphosphino)ethane
DMA	dynamic mechanical analysis
DME	1,2-dimethoxyethane
DMF	dimethylformamide
dmpe	bis(dimethylphosphino)ethane
DMSO	dimethylsulfoxide
DP_n	number-average degree of polymerization
DP_w	weight-average degree of polymerization
dppe	bis(diphenylphosphino)ethane
dppm	bis(diphenylphosphino)methane
DSC	differential scanning calorimetry
E_g	band gap energy
$\Delta E_{1/2}$	redox coupling
ESR	electron spin resonance
Fc	ferrocenyl group $-(\eta^5\text{-C}_5\text{H}_4)\text{Fe}(\eta^5\text{-C}_5\text{H}_5)$
fc	ferrocenylene group $-(\eta^5\text{-C}_5\text{H}_4)\text{Fe}(\eta^5\text{-C}_5\text{H}_4)-$
FESEM	field emission scanning electron microscopy
GPC	gel permeation chromatography
$[\eta]$	intrinsic viscosity
η_{sp}	specific viscosity
ΔH_{cryst}	lattice enthalpy

Hex	hexyl group
HOCO	highest occupied crystal orbital
HOMO	highest occupied molecular orbital
IR	infrared
ITO	indium tin oxide
IVCT	intervalence charge transfer
IVET	intervalence electron transfer
K_c	comproportionation constant
λ	wavelength
L	neutral 2-electron donor ligand
LED	light emitting diode
LMCT	ligand to metal charge transfer
LUCO	lowest unoccupied crystal orbital
LUMO	lowest unoccupied molecular orbital
MALDI-TOF	matrix-assisted laser desorption ionization – time of flight
M_n	number-average molecular weight
M_w	weight-average molecular weight
Mes	mesityl (2,4,6-trimethylphenyl) group
MLCT	metal to ligand charge transfer
NBE	norbornene
NIR	near infrared
NLO	non-linear optical
NMP	N-methylpyrrolidin-2-one
NMR	nuclear magnetic resonance
OBDD	ordered bicontinuous double-diamond
Oct	octyl group
OTf	triflate (trifluoromethylsulfonate) group
OTTLE	optically transparent thin-layer electrochemistry
PB	polybutadiene
PDI	polydispersity index
PDMS	poly(dimethylsiloxane)
Pen	pentyl group
PEO	poly(ethylene oxide)
PFP	polyferrocenylphosphine
PFS	polyferrocenylsilane
phen	1,10-phenanthroline
PI	polyisoprene
PMMA	poly(methylmethacrylate)
PPV	poly(phenylenevinylene)
PS	polystyrene
PSS	poly(styrene sulfonate)
PVFc	poly(vinylferrocene)
PVP	poly(vinylpyridine)
P2VP	poly(2-vinylpyridine)
P4VP	poly(4-vinylpyridine)

PVTPP	poly(vinyltriphenylphosphine)
PXRD	powder X-ray diffraction
py or pyr	pyridine
RIE	reactive ion etching
ROMP	ring-opening metathesis polymerization
ROP	ring-opening polymerization
σ (in Scm^{-1})	electrical conductivity
ΔS_{diss}	entropy of dissolution
SAXS	small-angle X-ray scattering
SBP	soybean peroxidase
SCE	saturated calomel electrode
SEC	size exclusion chromatography
SEM	scanning electron microscopy
SHG	second harmonic generation
SPM	scanning probe microscopy
STM	scanning tunnelling microscopy
T_c	crystallization temperature
T_{cl}	clearing temperature
T_g	glass transition temperature
T_{lc}	melting temperature to give a mesophase
T_m	melting temperature
TCNE	tetracyanoethylene
TCNQ	7,7,8,8-tetracyanoquinodimethane
TEM	transmission electron microscopy
terpy	terpyridyl
TGA	thermogravimetric analysis
THF	tetrahydrofuran
TMEDA	<i>N,N,N',N'</i> -tetramethylethylenediamine
TMS	trimethylsilyl group
Tol	toluene
tppz	tetrapyridylphenazine
UPS	ultraviolet photoelectron spectroscopy
UV	ultraviolet
VFc	vinylferrocene
vis	visible
VPO	vapour pressure osmometry
WAXS	wide angle X-ray scattering
XPS	X-ray photoelectron spectroscopy
$Z_{\text{c,w}}$	weight-average critical entanglement chain length

1

Introduction

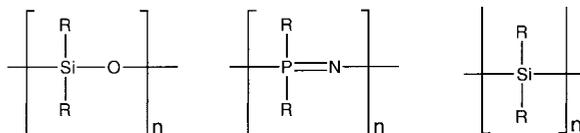
1.1

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].

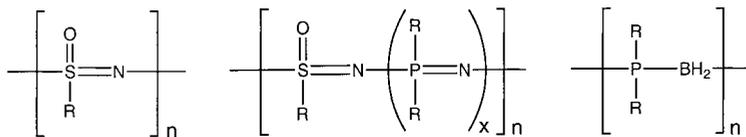


1.1

1.2

1.3

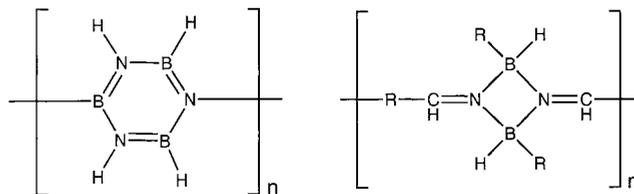
In the case of polymers based on non-metallic main group elements, the development of novel thermal, Lewis acid or base promoted, or transition metal-catalyzed polycondensation strategies that proceed with the elimination of small molecules such as $\text{Me}_3\text{SiOCH}_2\text{CF}_3$, Me_3SiCl , H_2 , 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].



1.4

1.5 $x = 2$
1.6 $x = 1$

1.7



1.8

1.9

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 ($1.0 < \text{PDI} < 1.2$) 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. 1.1 a). Examples of broad and narrow monomodal molecular weight distributions are shown in Fig. 1.1 b and 1.1 c, respectively.

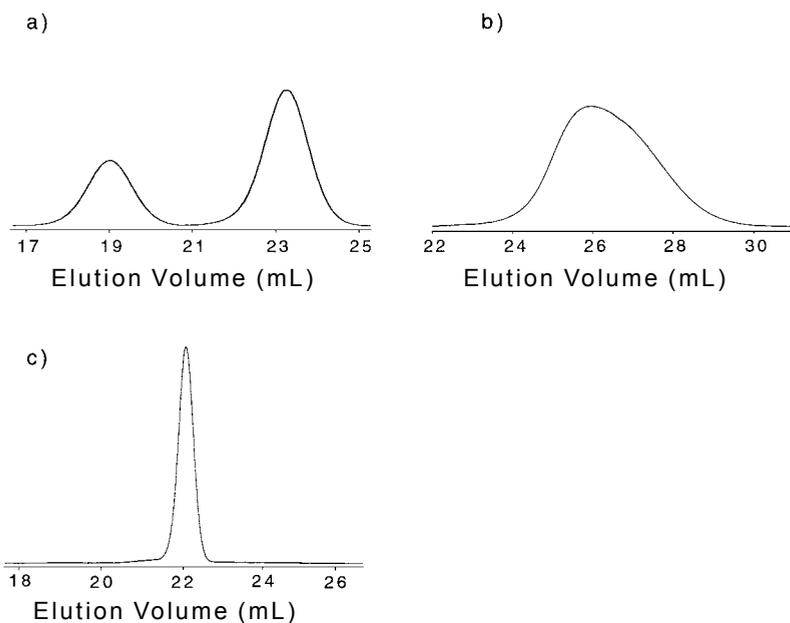
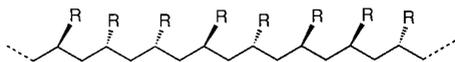


Fig. 1.1 Typical GPC traces showing (a) a bimodal molecular weight distribution, (b) a broad monomodal molecular weight distribution (PDI=2.3), and (c) a narrow monomodal molecular weight distribution (PDI=1.05). The x-axis shows the elution volume for the GPC instrument with molecular weight increasing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

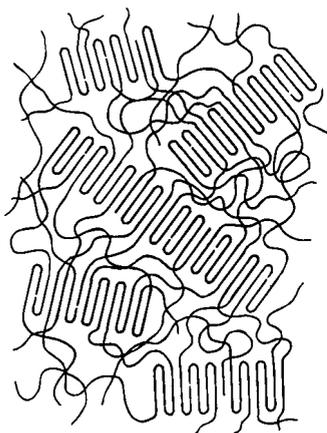
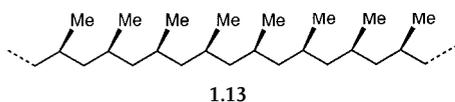
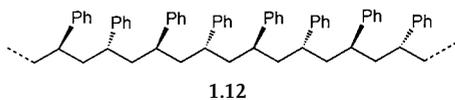


Fig. 1.2 Model of a semicrystalline polymer showing chain-folded crystallites embedded in an amorphous matrix (Reproduced from [37a]).

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.



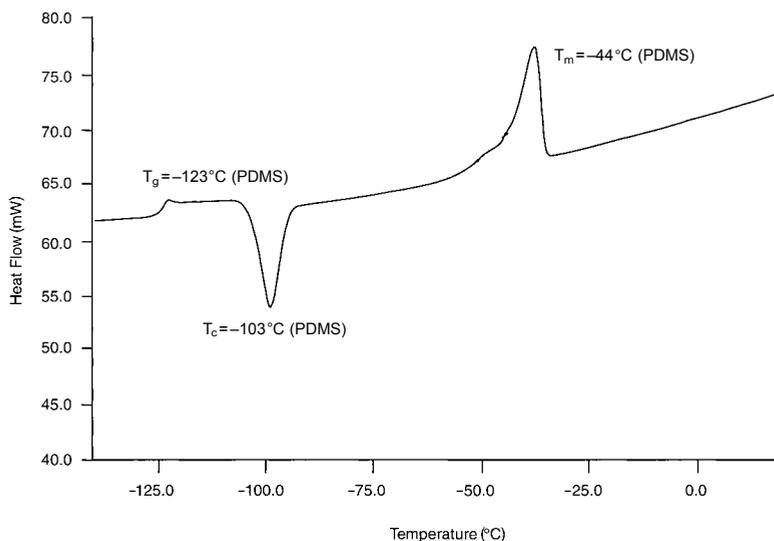
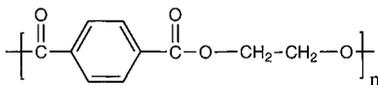


Fig. 1.3 A DSC trace showing a series of idealized thermal transitions (i.e. T_g , T_m , and T_c) for poly(dimethylsiloxane) (PDMS).

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 ($T_g \approx 100^\circ\text{C}$), 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_{ic}) 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.

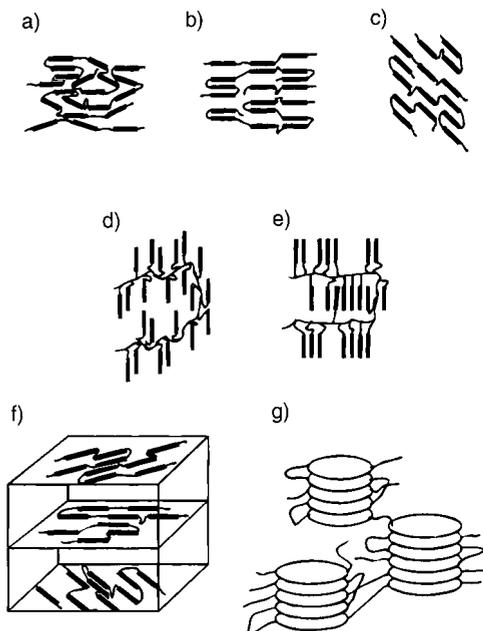


Fig. 1.4 Nematic and smectic main-chain liquid-crystalline polymers: (a) main-chain nematic, (b) main-chain smectic A, (c) main-chain smectic C, (d) side-chain nematic, (e) side-chain smectic A, (f) main-chain cholesteric, (g) main-chain discotic (Reproduced from [43]).

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-

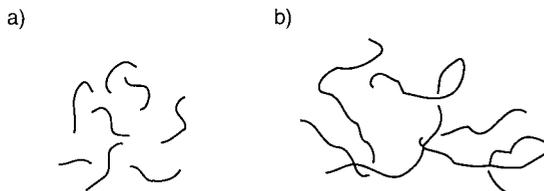


Fig. 1.5 (a) Oligomers, which do not entangle due to their short chains, and (b) chain entanglements in an amorphous high molecular weight polymer.

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-

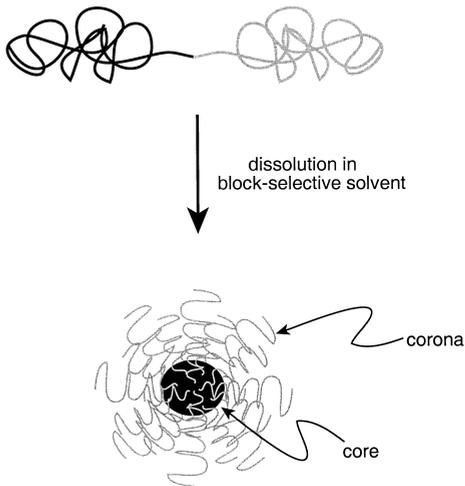


Fig. 1.6 Formation of spherical micelles from a block copolymer in a block-selective solvent.

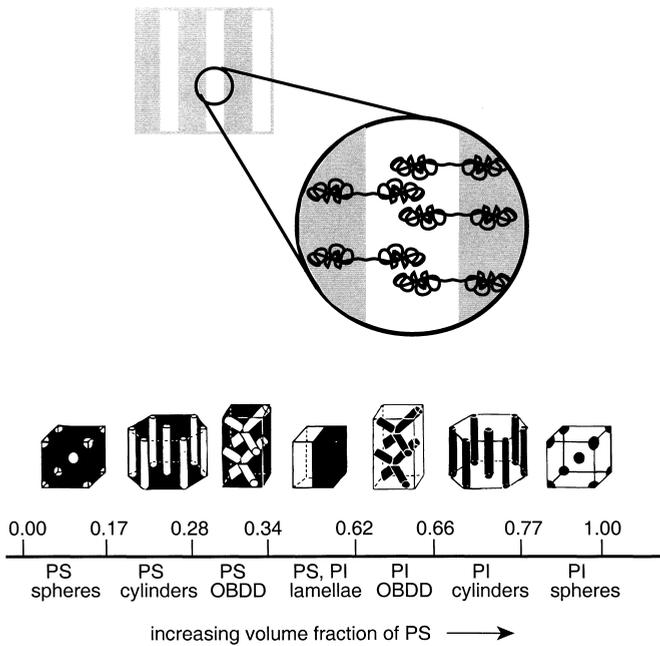


Fig. 1.7 Polystyrene-*b*-polyisoprene (PS-*b*-PI) solid-state morphologies as a function of increasing volume fraction of the polystyrene block (Adapted from [56]).

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 to 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).

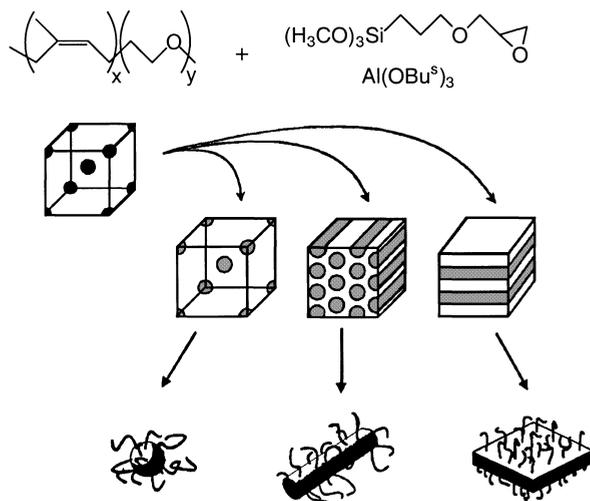


Fig. 1.8 Nano-objects with controlled shape and size from block copolymer mesophases: At the top left, phase-separated PI-*b*-PEO is shown, where the spheres consist of the PEO block. Subsequent dispersion and sol-gel hydrolysis of silicon and aluminum alkoxides in the PEO block leads to swelling of 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]).