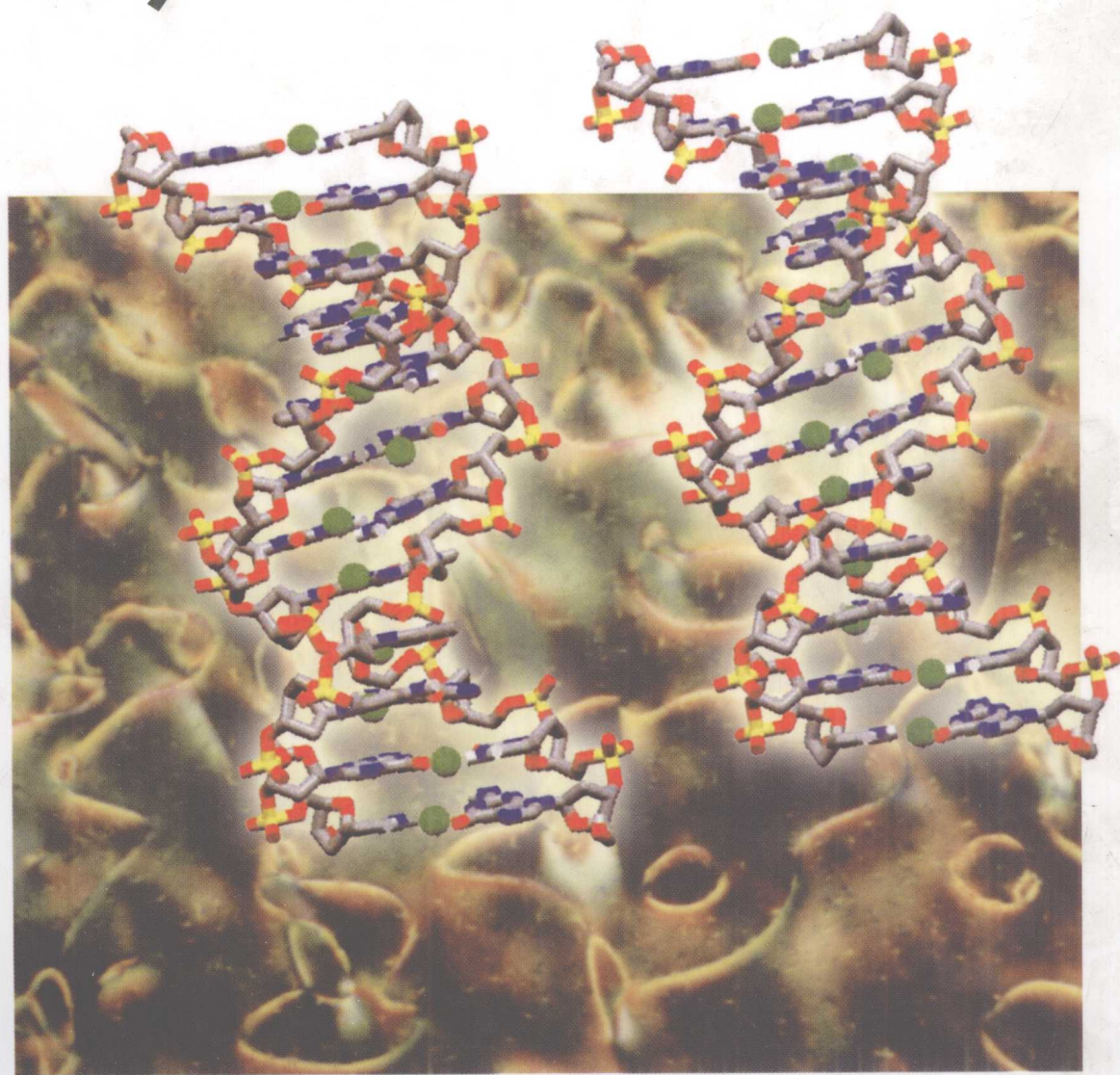Ian Manners

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 meso-
phase formed by a Pt polyyne (see Chapter 5,
section 5.2.3.2.)

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 metallopolymers 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

Contents

Abbreviations

A-*b*-B	diblock copolymer
A-*r*-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 -$(\eta^5\text{-}C_5H_4)Fe(\eta^5\text{-}C_5H_5)$
fc	ferrocenylene group -$(\eta^5\text{-}C_5H_4)Fe(\eta^5\text{-}C_5H_4)$-
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	N,N,N',N'-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
$Z_{c,w}$	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**
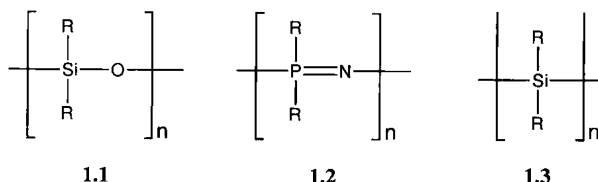
In the case of polymers based on non-metallic main group elements, the development of novel thermal, Lewis acid or base promoted, or transition metal-catalyzed polycondensation strategies that proceed with the elimination of small molecules such as $Me_3SiOCH_2CF_3$, Me_3SiCl, H_2, H_2O, and CH_4, as 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].

1.4   **1.5** x = 2   **1.7**
                  1.6 x = 1

1.8   **1.9**
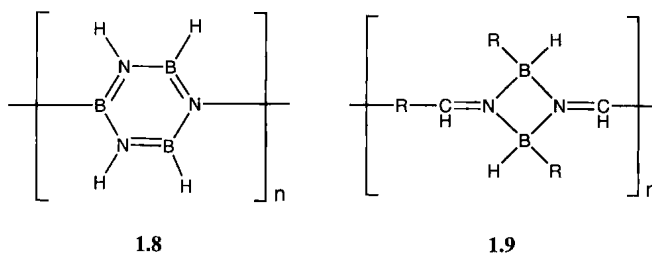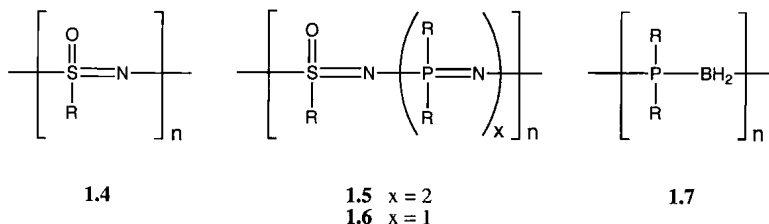
Many similar synthetic challenges exist in the area of polymers based on metallic elements. At the molecular level, metal chemistry is well developed. For example, the preparation of carefully designed, single-site transition metal catalysts has already had a dramatic impact on polymer science, particularly 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 < 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.
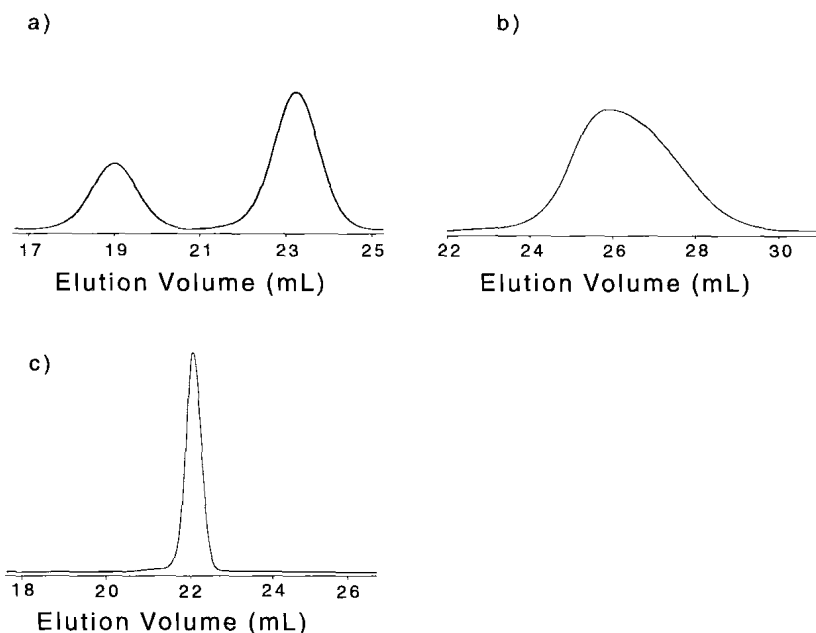
a)

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.
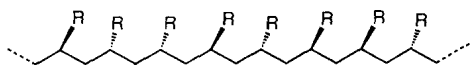
1.10 R = Ph
1.11 R = Me

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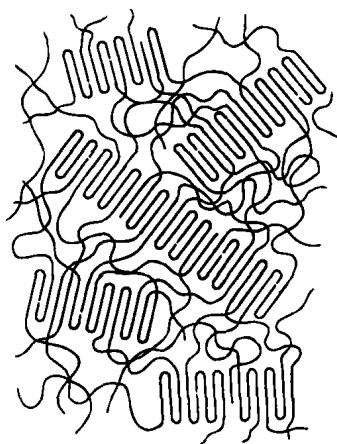
Fig. 1.2 Model of a semicrystalline polymer showing chain-folded crystallites embedded in an amorphous matrix (Reproduced from [37a]).

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