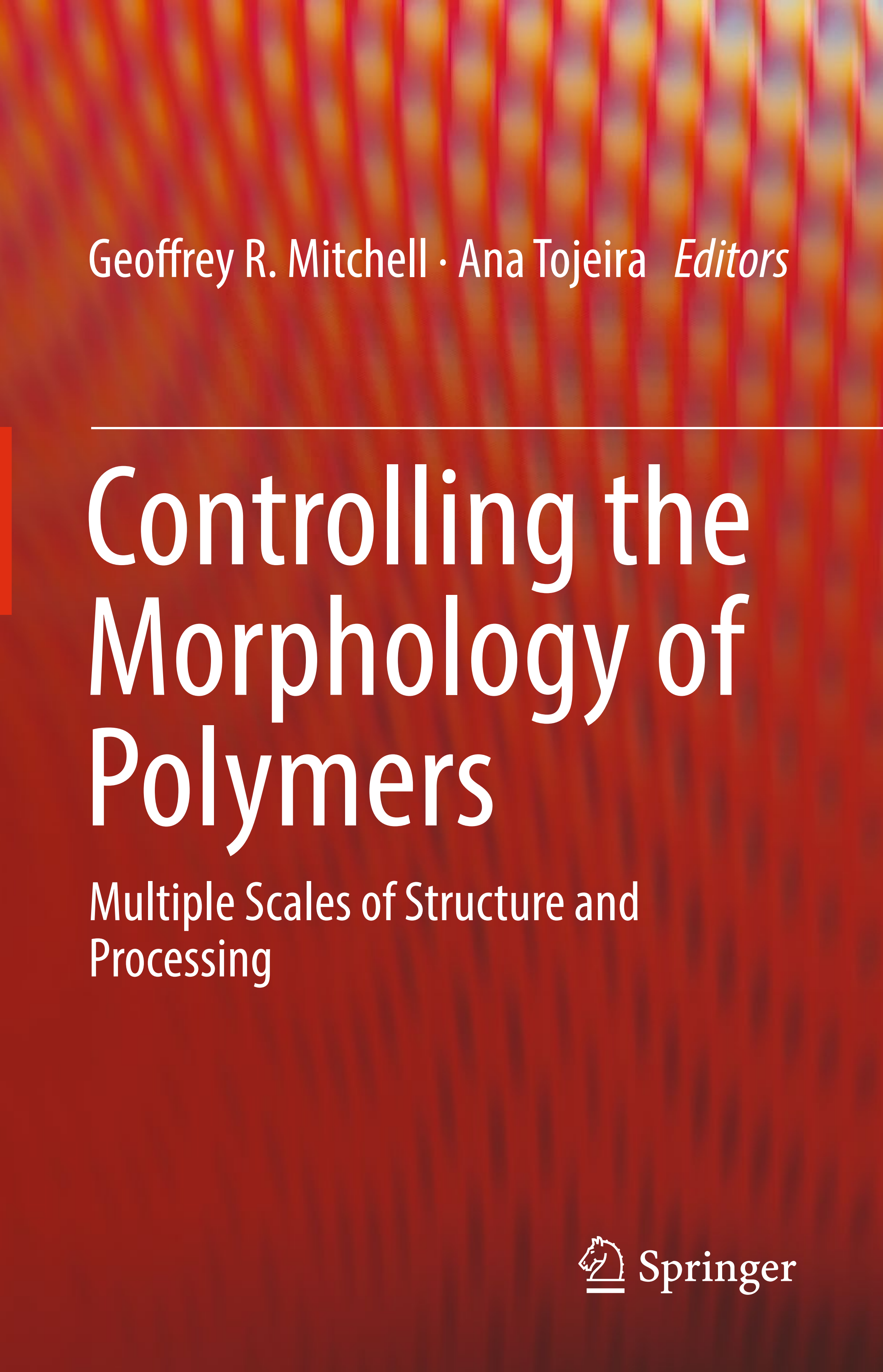


Geoffrey R. Mitchell · Ana Tojeira *Editors*

Controlling the Morphology of Polymers

Multiple Scales of Structure and Processing

Springer

Controlling the Morphology of Polymers

Geoffrey R. Mitchell • Ana Tojeira
Editors

Controlling the Morphology of Polymers

Multiple Scales of Structure and Processing

Springer

Editors
Geoffrey R. Mitchell
Product
Center for Rapid and Sustainable Product Development
Institute Polytechnic of Leiria
Marinha Grande, Portugal

Ana Tojeira
Product
Center for Rapid and Sustainable Product Development
Institute Polytechnic of Leiria
Marinha Grande, Portugal

ISBN 978-3-319-39320-9 ISBN 978-3-319-39322-3 (eBook)
DOI 10.1007/978-3-319-39322-3

Library of Congress Control Number: 2016947449

Printed on acid-free paper

The registered company is Springer International Publishing AG Switzerland
The Springer imprint is published by Springer Nature

To our families, for all the joy and inspiration.

Dedicated to the memory of Jill Mitchell (1948–2015).

Preface

The possibility of long-chain molecules was established at the start of the twentieth century through the pioneering work of Hermann Staudinger (1920), who was awarded the Nobel Prize in Chemistry in 1953 “for his discoveries in the field of macromolecular chemistry.” Much of the twentieth century was dominated by the ingenious work of synthetic organic chemists in producing polymers with particular chemical configurations and molecular lengths. The first to dominate the field were Giulio Natta and Karl Zeigler whose work led to the commercial production of stereoregular alpha olefins such as polypropylene (Natta 1967). The contribution of Karl Ziegler was the discovery of the first titanium-based catalysts. Giulio Natta used such catalysis to prepare stereoregular polymers from propylene. Both were awarded the Nobel Prize in Chemistry in 1963.

Other developments have built on these early steps. In the 1950s, scientists at Phillips Petroleum discovered that chromium catalysts are very effective for the low temperature polymerization of ethylene, which launched major industrial technologies. A little later, Ziegler discovered that the combination of titanium chloride and ethyl aluminum sesquichloride gave comparable activities for the production of polyethylene. Natta used crystalline α-titanium chloride in combination with triethyl aluminum to produce the first isotactic polypropylene. In the 1960s, BASF developed a gas phase, a mechanically stirred polymerization process for making polypropylene which led to the UNIPOL process, which was commercialized by Union Carbide to produce polyethylene. Later in the 1970s, magnesium chloride was discovered to greatly enhance the activity of the Ti-based catalysts. These catalysts are so active that the residual Ti is no longer removed from the product. They enabled the commercialization of linear low-density polyethylene (LLDPE) resins and allowed the development of noncrystalline copolymers. These developments and similar research have transformed plastics from an oddity only suited to Hula-Hoops into a major technological materials industry with a total global demand of over 200 million tonnes.

Functional polymers appeared in the second half of the twentieth century. Although polyaniline was first described in the mid-nineteenth century by Henry Letheby and polypyrrole derivatives were reported to be electrically conducting in 1963 by B.A. Bolto et al. (1963), substantial progress was not made with intrinsically conducting polymers until the pioneering work of Hideki Shirakawa, Alan J. Heeger, and Alan MacDiarmid who reported similar high conductivity in oxidized iodine-doped polyacetylene in 1977 (Shirakawa 1977). For this research, they were awarded the 2000 Nobel Prize in Chemistry "for the discovery and development of conductive polymers."

Liquid crystal polymers and elastomers (Donald et al. 2006), dendrimers (Hawker and Fréchet 1990), and block copolymers (Szwarc 1956) also appeared in the second half of the twentieth century. Today we can select polymers with many different properties and functions. Of particular current note is the development of photovoltaic devices which are beginning to show considerable promise. However, in the field of photovoltaics, researchers have found that it is not just the ingenuity of the molecule makers that delivers the efficiency but also controlling the morphology. Controlling the morphology is a major tool in polymer science and engineering. It enables chemically the same material such as polyethylene to be exploited to produce low-cost plastic bags as well as bulletproof vests.

This book sets out to embrace this control of morphology recognizing from the outset that the different scales of structure are connected. As Natta discovered the precise positioning of the methyl group in polypropylene leads to a high crystallinity and without precise positioning to a poor quality amorphous polymer used in roofing membranes, others have identified that the control of that crystallization process leads to clear packaging material which constitutes about half of the 60 million tonnes of polypropylene-based materials used in 2013.

Like the scales of structure, the contributors to this book are all interconnected in a myriad of ways. At the core, connecting many is the highly successful Reading Polymer Physics Group, later morphing into the Polymer Science Centre at the University of Reading. It was there that Alison Hodge, Robert Olley, and David Bassett optimized the permanganic etching process for revealing the morphology of semicrystalline polymers (Olley 1979). The advent of time-resolving X-ray scattering at synchrotron-based beamlines (Keates et al. 1994) has greatly added to the ability to follow in real time the development of structure and morphology during processing. Not all good things go on forever, and the University brought the curtain down on polymer physics at Reading in 2010 with the closure of the Department of Physics. With every closing door, another opens and so please check out controlling morphology during 3D printing in Chap. 7. The future is direct digital manufacturing as Mr. McGuire[1] might say.

---

[1] Mr. McGuire (played by Walter Brooke) is a character in the motion picture "The Graduate" who said in the movie "Plastics," followed by "There's a great future in plastics," to the graduate Ben Braddock played by Dustin Hoffman, which is one of all-time top 100 quotes judged by the American Film Institute.

We would like to thank all the authors for their contributions and their positive approach to this crosscutting project. It has been a pleasure to work with them all.

This work was supported by the Fundação para a Ciência e a Tecnologia (Portugal) through project PTDC/CTM-POL/7133/2014.

Marinha Grande, Portugal
Geoffrey R. Mitchell
Ana Tojeira

References

Bolto BA, McNeil R, Weiss DE (1963) Electronic conductions in polymers III electronic properties of polypyrrole. Aust J Chem 16:1090–1103
Donald AM, Windle AH, Hanna S (2006) Liquid crystal polymers. Cambridge University Press
Hawker, CJ, Fréchet JMJ (1990) Preparation of polymers with controlled molecular architecture. A new convergent approach to dendritic macromolecules. J Am Chem Soc 112(21): 7638–7647
Keates P, Mitchell GR, Peuvrel-Disdier E, Riti JB, Navard P (1994) A novel X-ray rheometer for in situ studies of polymer melts and solutions during shear flow. J Nonnewton Fluid Mech 52 (2):197–215
Keller A (1957) A note on single crystals in polymers: evidence for a folded chain configuration. Philos Mag Ser 8(2): 1171–1175
Letheby H (1862) J Chem Soc 15: 161
Natta G, Danusso F (eds) (1967) Stereoregular polymers and stereospecific polymerizations. Pergamon Press
Olley RH, Hodge AM, Bassett DC (1979) A permanganic etchant for polyolefines. J Polym Sci 17: 627–643
Shirakawa H, Louis EJ, MacDiarmid AG, Chiang CK, Heeger AJ (1977). Synthesis of electrically conducting organic polymers: halogen derivatives of polyacetylene, $(CH)_x$. J Chem Soc Chem Commun 16: 578
Staudinger H (1920) Über Polymerisation. Ber Deut Chem Ges 53(6): 107.
Szwarc M (1956) Living polymers. Nature 178: 1168–1169

Contents

Chapter 1
Scales of Structure in Polymers

Geoffrey R. Mitchell, Fred J. Davis, and Robert H. Olley

1.1 Introduction

The multi-valency of the carbon atom leads immediately to a rich variety of molecular structures including long-chain polymers. At the smallest scale, the chemical bonds are anisotropic but without appropriate molecular ordering, that anisotropy is not conveyed to the macroscopic scale which has a substantial impact on the properties. This chapter focuses on detailing these scales of structures and the types of ordering processes which are observed in polymer-based materials. We consider the mechanisms for the transformation of polymer melts by these ordering processes. Finally, we consider 'top-down' manufacturing processes which lead to 'ordering' on a scale larger than that intrinsic to the polymer material.

1.2 Types of Bonds

Although many inorganic systems may be considered to be polymeric, the term polymer is generally taken to refer to long chains of organic polymers. The importance of the high molecular weight is that it is this that controls their mechanical properties. The useful mechanical properties of a polymer arise from the increased magnitude of the bonding between molecules. This intermolecular

---

G.R. Mitchell (✉)
Center for Rapid and Sustainable Product Development, Institute Polytechnic of Leiria,
Marinha Grande, Portugal
e-mail: geoffrey.mitchell@ipleiria.pt

F.J. Davis
Department of Chemistry, University of Reading Whiteknights, Reading RG6 6AD, UK

R.H. Olley
EMLab, JJ Thomson Building, University of Reading Whiteknights, Reading RG6 6AF, UK

G.R. Mitchell, A. Tojeira (eds.), *Controlling the Morphology of Polymers*,
DOI 10.1007/978-3-319-39322-3_1

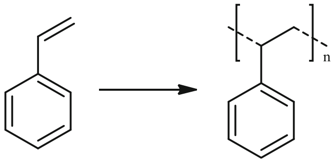
bonding is collectively classified as Van der Waals bonding although this terminology is often used just to describe the bonding from induced dipole-induced dipole forces (London Forces). In addition to the London dispersion forces, intermolecular bonding is provided by dipole-induced dipole forces, dipole–dipole forces and hydrogen bonding. In polymers with ionic groups, there may be ionic interactions. While London forces are generally considered to be the weakest of the interaction, because of their ubiquitous nature they tend to contribute more towards the overall intermolecular bonding (except in small molecules such as water). However, the presence of interactions additional to London forces results in increased strength; thus up to a molecular weight of 10,000 Da, polyethylene which has no permanent dipole is a waxy solid, while polyamides (with hydrogen bonding) are hard solids at weights as low as 1000 Da (Stevens 1990).

1.3 Types of Polymers

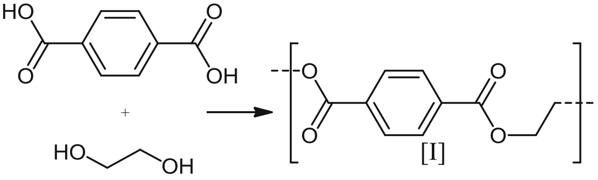
There are a number of different ways to classify polymers but perhaps the simplest division is between natural polymers (biopolymers) which include proteins (polypeptides), polysaccharides, and poly(nucleotides) and synthetic polymers which include polyethylene, poly(vinyl chloride) and nylon; some natural polymers are synthetically modified as in the formation of viscose rayon from cellulose or vulcanized rubber from natural rubber [largely poly(isoprene)].

Chemists generally classify synthetic polymers by their mode of synthesis: chain growth polymers are formed by the addition of single monomers to a growing chain, while step growth polymers are formed by the reaction of (for example) bifunctional monomers to form dimers, trimers, etc. which may react together to form larger molecules. An example of a chain growth polymerization would be the formation of polystyrene [Reaction (1.1)], while an example of the second is provided by poly(ethylene terephthalate) as shown in Reaction (1.2).

Reaction 1.1



Reaction 1.2



Chain-growth polymers are often formed from vinyl systems ($CH_2{=}CHX$) and represent some of the most common commercial polymers; examples include

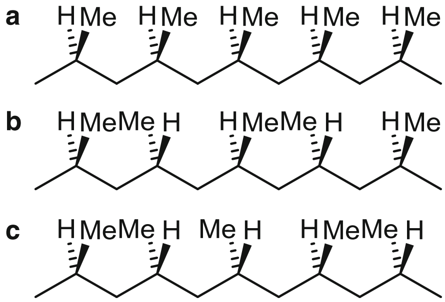


Fig. 1.1 Polymer tacticities for vinyl polymers (**a**) isotactic (**b**) syndiotactic (**c**) atactic (heterotactic)

Fig. 1.2 Schematic of copolymer systems: (**a**) homopolymer; (**b**) alternating copolymer; (**c**) random copolymer; (**d**) block copolymer; and (**e**) graft copolymer

polyethene, polypropene, poly(methyl methacrylate) and poly (vinyl chloride). One particular feature of these polymers is that for all systems except ethene (X=H), the resulting polymers have a stereogenic centre, resulting in a range of arrangements of the side groups, such arrangements are described in Fig. 1.1. The normal atactic (or random) arrangement might be expected from simple processes such as free-radical polymerization, more regular structures such as isotactic and syndiotactic poly(propene), are usually produced by organometallic catalysts such as the Ziegler–Natta catalyst (Stevens 1990). In general, the more stereoregular polymers have a greater tendency towards crystallization, and as such are often valued for their enhanced mechanical properties.

The repeat unit for poly(ethylene terephthalate) ([I] Reaction (1.2) above) is built up from two chemical units, but the polymer is a continuous repeat of this structure. In many cases, the structure of a polymer is modified by the addition of another monomer unit during the polymerization process, a process known as copolymerization. This for a vinyl polymer system, for example, styrene could be copolymerized with methyl methacrylate. Such copolymers can be arranged in different as shown in Fig. 1.2 and each type of material may show interesting or unique properties. For example, block copolymers may show microphase separation of the incompatible blocks of copolymer, and this can produce for example materials useful as photonic band-gap materials (Urbas et al. 1999) (See Chap. 10.)

1.4 Types of Materials

In addition to copolymerization described above, there is considerable interest in the control of polymer architecture. As this may have a considerable influence on the behaviour of polymers as materials. Thus, polymers may be linear (Fig. 1.3a), or branched (Fig. 1.3b) or may for more complex structures such as a star arrangement (Fig. 1.3c) or more sophisticated dendrimer arrangements. Some of these more complex architectures pose considerable challenges to the organic chemist in terms of reagents and equipment (Hadjichristidis et al. 2000), while others, for example, the introduction of cross-links, can be achieved using technically quite simple methodologies. Cross-linked polymers are an important class of materials in themselves and provide another classification, namely thermoplastics and thermosets; The former are those which melt and flow, the latter are materials which cannot melt or dissolve and are built up of cross-linked polymer chains.

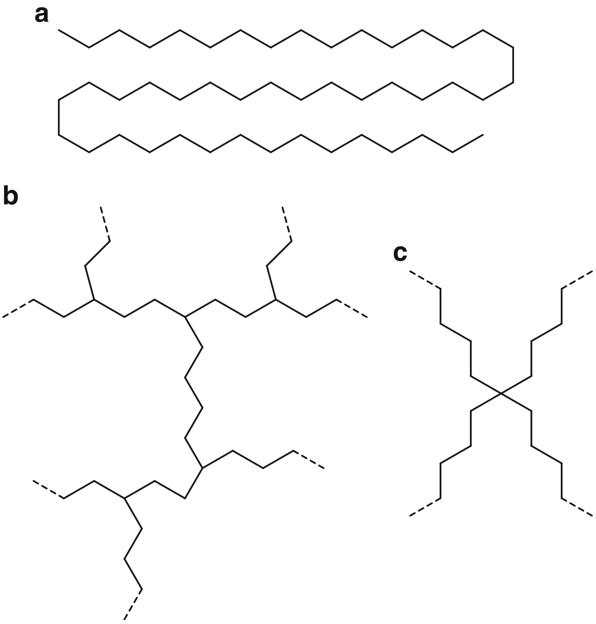


Fig. 1.3 Examples of polymer architecture: (**a**) linear; (**b**) branched; and (**c**) star structure

1.4.1 Thermoplastics

In terms of production of polymeric materials poly(ethene) dominates with typically 30 % of polymer production worldwide, other significant materials are poly (propene), and poly(styrene) and poly (vinyl chloride), though the latter has prompted considerable environmental debate, in terms of the toxicity of the monomer, the use of plasticisers in the products (particularly those which come into contact with children) and the production of dioxins in the ultimate disposal by pyrolysis. The major advantage of the general class of thermoplastics is that they soften and flow on heating and thus can be processed using a range of simple methodologies, which rely on the solidification of the melt into a particular form. Examples of processing methodologies include blow moulding, injection moulding, extrusion and spinning (Stevens 1990). The ability to process the polymer through melting or (less usually) through dissolution also allows for the polymer to be recycled although in this regard additives either added for appearance as stabilizers or for improved properties may influence the range of options possible.

As thermoplastics do not contain covalent bonds between chains the mechanical properties of the resultant polymers are highly dependent on the intermolecular forces holding neighbouring chains together (vide supra). That being said it is the presence of crystalline regions which often produce the high mechanical strength of many polymeric materials. Thus, careful control of polyethene morphology can result in extremely high modulus materials (Ward and Hine 2004). It should also be noted that while crystallinity can impart high mechanical strength through the close regular alignment of neighbouring molecules, the presence of amorphous regions also provides some elasticity and impact resistance.

1.4.2 Thermosets

Thermosetting polymers are those systems where a network of cross-linking between chains means that the polymer cannot be dissolved or liquefied on heating. In lightly cross-linked system, there may be considerable deformation allowed at the right conditions as in the stretching of an everyday rubber band, but ultimately the bonding of neighbouring chains restricts their translational motion. In highly cross-linked systems, the polymer may have considerable dimensional stability. In both cases, the ultimate form (leaving aside issues of applied forces) is determined at the time of cross-linking and to form useful products the cross-linking process must form part of the manufacturing process. One of the first commercially important synthetic polymers was Bakelite® (Baekeland 1909) which is a phenol formaldehyde resin, since these are the two components involved in its manufacture (Fig. 1.4). This material was extremely popular in the first half of the twentieth century for the production of a range of domestic and electrical goods.

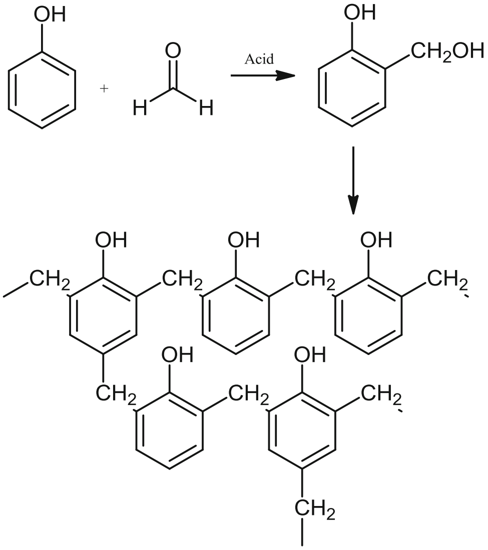
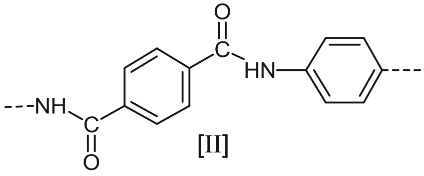


Fig. 1.4 Synthesis of the thermosetting material Bakelite®

1.4.3 Composites, Micro-Fillers, Nano-Fillers

Increasingly a range of applications require polymers with enhanced performance. This has led to a further classification, namely between engineering and commodity polymers. The latter are those that are produced in high quantities as discussed in Sect. 1.4.1; the former are generally more expensive materials, which are manufactured on a smaller scale but are valued for certain superior properties, such as increased mechanical strength or thermal stability. Perhaps the best known example of an engineering plastic is Kevlar [II], which finds use in a range of applications including body protection.



[II]

Notwithstanding the remarkable properties of materials such as Kevlar, modern engineers are constantly looking for improved performance. One of the most successful areas in this regard is the development of composites; such materials are manufactured in such a way that the final material has superior properties to the sum of its constituents. For example, fibres of Kevlar, glass or carbon are used to reinforce epoxy resins. Increasingly developments are focusing on more sophisticated materials; for example, poly (ether ether ketone) can replace epoxy as the matrix, and more complex reinforcing materials have been used for example carbon nanotubes (Coleman et al. 2006). Indeed, the new Boeing ‘Dreamliner’ airplane introduced in 2014 is structural based around composite materials.

1.5 Types of Order

1.5.1 *Crystalline*

The crystalline state is a state of matter ideally characterized by three-dimensional, long-range order on an atomic scale. A crystallizable polymer is polymer that is able to partially crystallize (IUPAC 1997). Large single crystals of polymers are not observed except in the case of polydiacetylenes as they can be prepared via a topochemical polymerization of the single crystals of the monomer. Single crystals of polymers such as polyethylene can be prepared from solution (Geil 1963), whereas polymers crystallized from the melt phase contain both crystalline regions and uncrystallized amorphous material. The crystalline regions are in the form of chain folded lamellae (see Sect. 1.6).

1.5.2 *Liquid Crystalline*

A liquid crystal polymer is a material that, under suitable conditions of temperature, pressure, and concentration, exists as a liquid crystal mesophase (IUPAC). Liquid crystal phases are those characterized by a high level of orientational order in the absence of positional order as observed in the crystalline state. The nematic state is observed with rod-like molecules with a common axis of orientation as shown in Fig. 1.5.

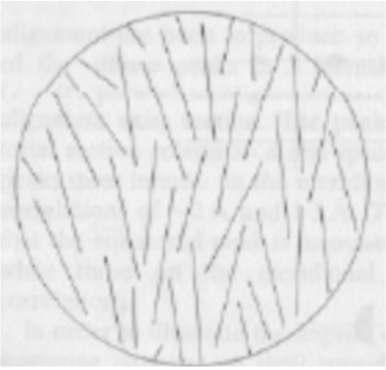


Fig. 1.5 Schematic representation of the molecular order present in the nematic liquid crystal phase. The *line* represents the rod-line molecules

In a polymer, the rod-like structures can be attached as side groups—side-chain liquid crystal polymers or with the skeletal backbone—main chain liquid crystal polymers (Donald et al. 2006). The latter usually exhibit liquid crystal characteristics at elevated temperatures, while some side-chain liquid crystal polymers exhibit liquid crystalline order at room temperature. A number of more ordered smectic phases can be observed as well as chiral, nematic, and smectic phases (Donald et al. 2006).

1.5.3 Amorphous

The amorphous state is a state of matter characterized by the absence of long-range molecular order. Polymers exhibit this disordered but solid state either as a consequence of a thermal history which includes cooling from the melt state at a rate which inhibits crystallization or through the presence of disorder along the polymer chain such as present in random copolymers or atactic systems. Typically glassy polymers are optically clear and a key characteristic is the glass transition temperature. The transformation in molecular dynamics from that of a polymer melt to those of the glassy state does not occur over a very short temperature range as in the case of a first-order phase transition such as melting. Rather, it extends over several Kelvins and a plot of heat capacity of thermal expansion coefficient exhibits a smooth step. The glass transition temperature is defined by convention in which the heating rate is a critical factor.

1.5.4 Blends and Mixtures

As with other material systems, different types of polymers can be mixed to provide control of properties. A polymer blend is a macroscopically homogeneous mixture of two or more different species of polymer [IUPAC]. The low entropy of mixing of polymers due to the high molecular weight means that different polymers do not readily form a homogeneous blend; rather they form mixtures with a phase separated structure whose morphology will depend on the preparation route. The presence of a solvent further complicates matters.

1.6 Structuring Processes

1.6.1 Crystallization

It may come as a surprise to many that a large number of the common plastic items in everyday use are semicrystalline. As the IUPAC definition states, ‘A crystallizable polymer . . . is able to partially crystallize.’

Crystallinity in polymers was first observed by X-Ray Diffraction even before these materials were understood to be polymers. Prominent examples were polysaccharides, especially cellulose (Herzog et al. 1920) and stretched natural rubber (Katz 1925). This was before Staudinger's macromolecular concept was widely accepted (Morawetz 1995). By the time synthetic crystalline polymers such as polyethylene (in 1933) and nylons (in 1935) were developed, it was generally acknowledged that the unit cell of a polymer crystal was based on repeating monomer units, rather than on the whole molecules.

Polymer crystallization is dominated by the process of untangling molecules and then straightening them onto the crystal growth face. Because of this, it is a comparatively slow process compared with crystallization of simple molecular species, and it may require supercooling by tens of Kelvins to occur at a significant rate.

Not all polymers can crystallize. Polyethylene does, but atactic polystyrene (the common form) does not. Though the specialized syndiotactic and the more common isotactic forms do, albeit into completely different crystal forms (de Rosa and Auriemma 2013). Isotactic polypropylene and many nylons commonly crystallize into more than one crystal type, and polyethylene terephthalate (PET), a polyester, is commonly found in a glassy form in soft drinks bottles but crystallizes readily on appropriate thermal treatment.

1.6.1.1 Lamellae to Spherulites

Up to about 1955, the only widely held model of semicrystalline polymer morphology was the **fringed micelle model**. In this, polymer crystallites were composed of small stacks of parallel chains, outside of which chains wandered between crystallites rather than folding back into the same bundles. This model, however, did not fit well with the observation (Bunn and Alcock 1945) that in polyethylene spherulites, the molecular chains lay perpendicular to the radial growth direction of the spherulites, nor with their suggestion that the crystallites might grow radially like the thin plate-like crystals of high molecular weight *n*-paraffins.

A great advance in the understanding of polymer crystals came with the discovery that polyethylene would crystallize from solution in hot xylene to give thin crystals, known as **lamellae**, which could be observed under the electron microscope. Electron diffraction showed that the chains ran more-or-less perpendicular to the plane of the crystals, and subsequent investigation has shown that this is the normal mode of crystallization for almost all polymers. These were reported by several workers, among whom Keller (1957) deduced that the chains must fold at the top and bottom surfaces of the crystals, so that the chain re-entered, going in and coming out of both surfaces. This had been suggested (Storks 1938) from observations of thin films of gutta-percha, which however did not contain isolated individual crystals.

Polymers on the trigonal and tetragonal systems tend to form lamellae based on their crystal system, hexagonal in the case of iPS and POM, square in the case of

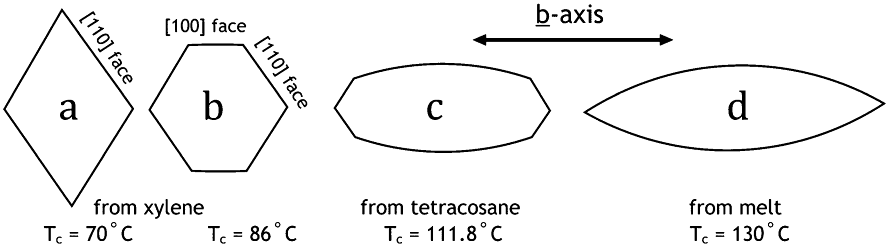


Fig. 1.6 Shapes of polyethylene crystals grown from solution or melt under the conditions indicated

poly4-methyl pentene-1. Polyethylene on the orthorhombic system, when grown from solution, does produce lozenges with [110] faces as at **a** in Fig. 1.6. When grown at the higher temperatures truncated lozenges **b** are formed with [100] faces at each end. For progressively poorer solvents and at higher temperatures **c**, the [110] faces become increasingly dominant and curved, while from the melt **d** only these [100] faces are observed. This is consistent with the observation that in polyethylene, the radial growth direction of spherulites is along the b-axis (Bassett et al 1979).

At the same time, as solution crystals were observed by electron microscopy, Fischer observed screw dislocations in electron micrographs of melt crystallized polyethylene-banded spherulites (Fischer 1957), which have since been shown to be the primary mode of branching in polymer lamellae. This, together with splaying out of the plane of the original lamellae, forms the mechanisms of three-dimensional growth into spherulites. From small initial lamellae, there develop objects which are generally called axialites because they were thought to be axially symmetrical like a wheatsheaf with splaying stalks. Where the initial crystal is of high symmetry, as in the hexagonal lamellae of isotactic polystyrene, intermediate stages of growth are often called hedrites because of their resemblance to mathematical polyhedra. These early objects, however, appear very different according to which direction they are viewed: this is particularly clear in the case of isotactic polystyrene (Bassett and Vaughan 1985) and polypropylene (Olley and Bassett 1989).

The wide variety of the morphologies observed, both in crystals formed from solution and from the melt, including precursors to spherulites and more developed versions especially banded spherulites, are presented in ‘Structure of Polycrystalline Aggregates’, together with discussion of current theories of their formation, by Crist (2013).

1.6.1.2 Crystal Growth Rates

Much effort has gone into the determination of crystal growth rates in polymers. In practice, this involves determining how fast spherulites grow, so what is determined is the fast growth direction for the polymer in question, for example, the b-axis in polyethylene and the a*-axis for the common α-form of polypropylene. This has led to a large number of theories of crystal growth in polymers.

1.6.1.3 Primary and Secondary Nucleation

One early theory which is still widely applied is that of Hoffman and Lauritzen, in which a nucleus forms on a flat crystal surface. First proposed in 1961, in 1973 it was extended to include regimes of crystallization, initially two (Lauritzen and Hoffman 1973), later extended to three. In Regime 1 (Fig. 1.7), a single molecular chain overcomes a nucleation barrier to settle on the growth surface, producing a step from which further chains can quickly be added. In Regime II at lower temperature, several chains and sideways development are simultaneously present on the same surface, and in Regime III growth is extending outward before completion of the first new layer. In the initial presentation of regime theory, there was observed an apparent correlation of ‘axialitic’ growth with Regime I and more classical spherulitic growth in Regime II; this was later shown to be a consequence of the different times available for chain fold reorganization in the two regimes (Abo El Maaty and Bassett 2006). The theory was modelled on flat crystal growth surfaces, and received a strong challenge from the discovery of curved growth (Organ 1986). A strong attempt was made to bring both nucleation and curvature into line (Point and Villers 1992) and modifications continued (Armistead and Hoffman 2002). A state-of-the-art review (Cheng and Lotz 2005) provides an excellent starting point for further reading. Some recent theories dealing with both growth rate and crystal thickness involve the intervention of a mesophase as the first stage of crystallization: (Keller et al. 1994; Strobl 2005).

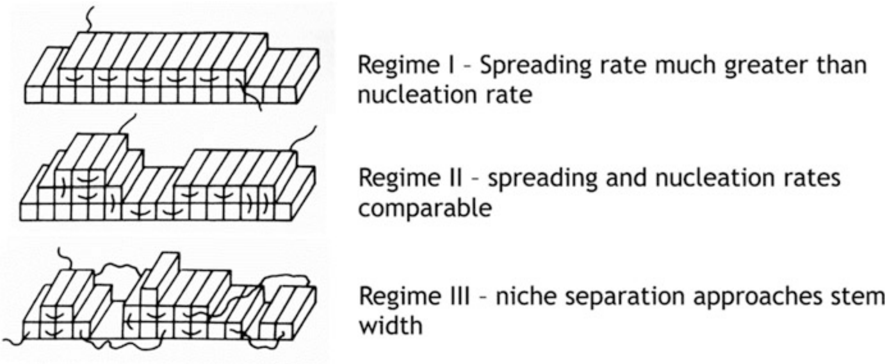


Fig. 1.7 Diagram of crystal growth in Regimes I to III according to the Hoffman–Lauritzen theory

1.6.1.4 Folding Theories

The question of folding resolves itself into three parts: (1) the topology of folding, whether chain folds back adjacent to itself, (2) the packing in the fold surface region, particularly how liquid or solid it may be, and (3) how frequently does the chain fold, a reciprocal space way of looking at how is lamellar thickness determined?

Regarding the first question, adjacent re-entry of stems into the same lamella is only approximated in solution crystals and material crystallized very slowly from the melt. On faster crystallization, stems are more likely to re-enter the same basal surface at some distance from where they emerged, known as the ‘switchboard’ model. Moreover, unless crystallization is slow enough for a molecule to reconfigure themselves in the melt by the process known as reptation, only local reorganization is possible as in the solidification model pictured below (Fig. 1.8) (Dettenmaier et al. 1980). The shape of the molecule as a whole will not be grossly changed, and so its radius of gyration will not be very different from what it was in the melt. Neutron scattering experiments do indeed show that radius of gyration is very little changed on fast crystallization from the melt, but in solution crystallized lamellae it is of the same order as the lamellar thickness, even for long molecules (Sadler 1984).

From the melt, faster crystallization is known to produce a greater proportion of ‘amorphous’ in relation to crystalline material, to which an change to switchboard-like rather than adjacent re-entry is only one of several contributory factors. Where there is a large amount of inter-lamellar material, there is the possibility of much of this being similar in properties to the melt. However, near the crystal surface its motion is constrained, and its reduced mobility compared to the rubbery behaviour

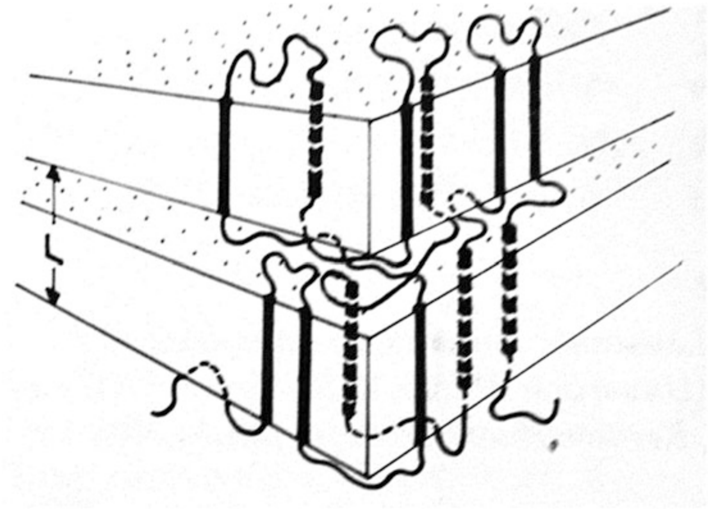


Fig. 1.8 Crystallization according to the solidification theory (Dettenmaier et al. 1980)

of material further away from the lamellae is to be expected. It is observed as an ‘interphase’ measurable by ^{13}C NMR (Kitamaru et al. 1986), and its existence as a rigid-amorphous’ phase in poly(oxy-l,4-phenyleneoxy-l,4-phenylenecarbonyl-1,4-phenylene) (PEEK) though thermal analysis (Cheng et al. 1986). Fold surfaces do not necessarily remain as they are laid down, but in polyethylene are able to reorder subsequent to initial crystallization, this process determining the characteristic S-shaped cross section of lamellae formed at all but the highest crystallization temperatures (Abo El Maaty and Bassett 2001).

1.6.1.5 Computer Modelling Theories

Lamellar thickness, folding, and growth rate are all interconnected phenomena, and in order to understand the crystallization mechanism as a whole, a wide variety of methods, mostly based on molecular dynamics and related methods have been developed to simulate polymer crystallization. For an excellent discussion, on these the reader is directed to Chap. 4 and (Rutledge 2013).

1.6.1.6 The Bell Curve

In terms of bulk polymers, we have talked so far about crystallization ‘from the melt’: however, if a polymer is cooled rapidly enough from the melt, it may not crystallize but instead form a glass. For polymers in general, the crystallization rate as a function of temperature passes through a maximum (Fig. 1.9). The first report

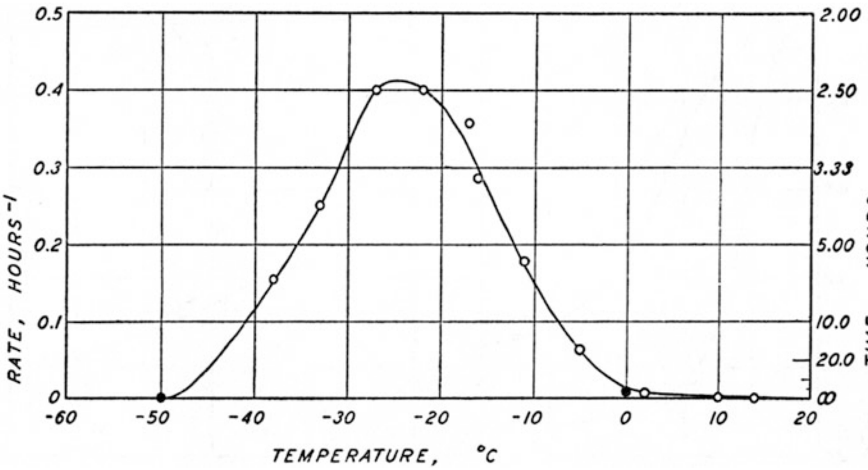


Fig. 1.9 Rate of crystallization of natural rubber over a range of temperatures, according to Wood and Bekkedahl (1946)

of this is attributed to Wood and Bekkedahl (1946) of dilatometric measurements of the crystallization of unvulcanized rubber in an unstretched state.

The best known case of this behaviour is polyethylene terephthalate (PET), which is most commonly encountered in the amorphous state as bottles. Whether heated from the glass or cooled from the melt, it will crystallize more rapidly the further below the melting temperature or the higher above the glass transition temperature, reaching a maximum from either side. Crystallization in polymers is a nucleation-controlled phenomenon: the graph above refers to overall degree of crystallinity, but if growth rate of spherulites is plotted, the maximum will be moved to somewhat lower temperature, since nucleation is denser at lower temperatures. The increase in growth rate while cooling from the melt is a thermodynamically based phenomenon, whereas the increase from the glass transition temperature is a result of decreasing viscosity.

In polymers which crystallize very rapidly, particularly polyethylene and isotactic polypropylene homopolymers, it is not feasible to cool quickly enough to obtain a glass (though with very thin films for some copolymers may be) so the full crystallization curve cannot be obtained for these materials.

1.6.1.7 Nucleation

When crystallizing a polymer such as polyethylene or polypropylene isothermally, it is generally found that the number of spherulites nucleated in a given volume at close to the melting temperature at low supercooling is relatively few, but if the temperature of crystallization is reduced, more spherulites are nucleated. A similar effect is observed where the polymer is crystallized non-isothermally during cooling, with faster cooling rates leading to overall lower crystallization temperatures. One advantage of higher crystallization temperature that may be desired is the greater lamellar thickness and higher degree of crystallinity leading to a stiffer material. Nucleating additives may be used to bring this about, along with economy due faster processing times. The lamellae which constitute spherulites are generally birefringent, so the radial orientation of lamellae in spherulites generally makes polymer objects translucent or even opaque. (Poly 4-methyl pentene-1 is an exception since the refractive indices of its optic axes are almost the same; moreover, the density of crystal and amorphous phases is very similar.) Since spherulites are optically anisotropic reduction of spherulite sizes to sub-micron levels will reduce optical scattering: in such uses the nucleating agents are known as clarifiers: clarified PP articles may be effectively as clear as glassy polystyrene (see Chap. 5). For a comparison of different nucleating agents, see Fillon et al. 1993.

1.6.1.8 Crystallization in Practice

Polymer melts are not molecularly homogeneous. Even in homopolymers, there is polydispersity of molecular weights, while with copolymers there is almost always a variation of comonomer content between different molecules. In homopolymers, fractionation by molecular weight during crystallization can occur, with longer molecules from the original dominant structure and short ones the subsequent infilling subsidiary structure. Much more pronounced effects are found in copolymers, where on continuous cooling molecules with less comonomer content crystallize first at higher temperatures, a range of subsequent melting points can be generated (Chen et al. 2004).

1.6.1.9 Crystallization and Orientation

One factor not taken into account so far is orientation of the polymers. The effect on crystallization can occur in many ways. Transient crystallization on stretching of rubbers, observed for natural rubber by Katz (1925), is also found in certain synthetic rubbers (Toki et al. 2004).

A study by Zachmann and Gehrke (1986) of crystallization of oriented amorphous films shows that in PET orientation leads to faster crystallization and in polyamide-6 leads to formation of the γ-rather than the common α-phase.

The subject of crystallization from stressed melts has been reviewed (Kumaraswamy 2005) and one frequent occurrence in the time sequence of this crystallization is the formation of row nuclei which give rise to structures known as ‘shish-kebabs’. Polypropylene is the polymer best known for its remarkable propensity for forming row structures, which often contain considerable amounts of β-phase material (Olley et al. 2014), and are a major feature of the skin-core structure of injection-moulded polypropylene (Shinohara et al. 2012), but they are also found in polyethylene (An et al. 2006), isotactic polystyrene (Azzurri and Alfonso 2008), poly(phenylene sulfide) (Zhang et al. 2008) and polylactide (Xu et al. 2013).

Row structures are an instance of amplification of orientation in a specimen by crystallization onto oriented nuclei, but the other extreme is represented by highly oriented fibres, especially those of ultra-high modulus polyethylene (Abo El Maaty et al. 1999).

1.6.2 Microphase Separation and Block Copolymers (BCP)

In 1956, it was found (Szwarc 1956) that anionic ‘living’ polymerization could generate block copolymers. (These were not the first block copolymers to be prepared: in 1937 Otto Bayer had synthesized polyurethanes, and Pluronic® surfactants consisting of blocks of polyethylene oxide and polypropylene oxide were patented in 1954.) This method of synthesis went commercial when in 1961 Shell scientists, working to increase the green strength of polyisoprene rubber for tyre applications, discovered that by adding styrene monomer sequentially to the anionic polymerization of polyisoprene, strong thermoplastic elastomers were produced which required no vulcanization yet could be moulded into different shapes with heat. The (typically) 20 % of polystyrene (PS) would segregate into small spherical regions, effectively vulcanizing the material, in place of chemical cross-links. (These materials were called Kraton® after Kratos, the Greek god of strength and brother of Nike.) In a sense, these were 'effectively composite' materials, similar in principle to semicrystalline polyethylene but with rubber elasticity in the 'soft' phase and the glass transition of the PS allowing the material to be stable up to the boiling point of water, whereas a PE of 20 % crystallinity would melt well below this.

Although we do not know the details of commercial synthesis, in the laboratory such a polymer would be synthesized in solution in a solvent such as tetrahydrofuran (Douy and Gallot 1972) which would be a one-phase system. On removal of solvent, a simple mixture of polystyrene and polyisoprene would segregate into a two-phase blend with a coarse structure and poor mechanical cohesion, due to low entropy of mixing. When the two materials are joined in one molecule, however, the two phases are very limited in migration, and form a microscopic structure with the two segregated phases in close connection. An increase in domain size is promoted by the drive to minimize the surface area–volume ratio of the structure, which would reduce the interfacial free energy. However, growth is limited by the localization of the junction between chain segments at the domain boundary, and increasing domain size would also stretch the chains from their random coil (Gaussian) configurations leading to a reduction in entropy.

From 1970 reports started appearing that the segregated regions in block copolymers were organized in lattices of spheres, cylinders or lamellae, depending on the relative volumes of the components. Electron micrographs showing patterned spheres (Lewis and Price 1969), lamellae and cylinders (Mayer 1974) and (Douy and Gallot 1972). Such techniques are usable only with thin films or thin cryosections, and generally require selective staining with reagents such as osmium tetroxide or ruthenium tetroxide.

The electron micrographs in Fig. 1.10 show the (left) (100) and (right) (111) projections of the BCC macrolattice for a styrene-butadiene diblock

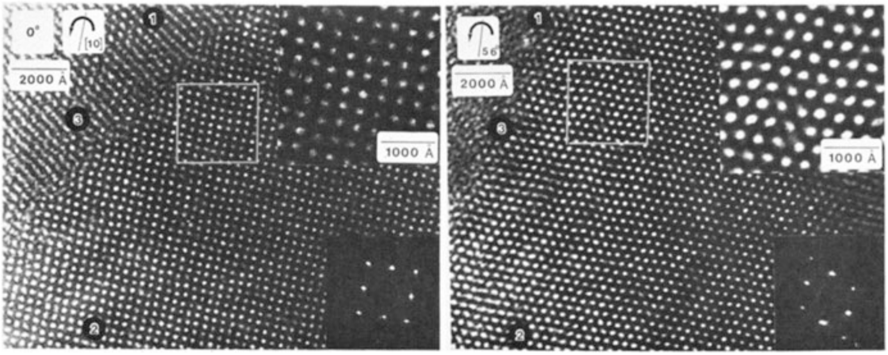


Fig. 1.10 Electron micrographs of two projection of the BCC microlattice of a styrene-butadiene block copolymer (Thomas et al. 1987)

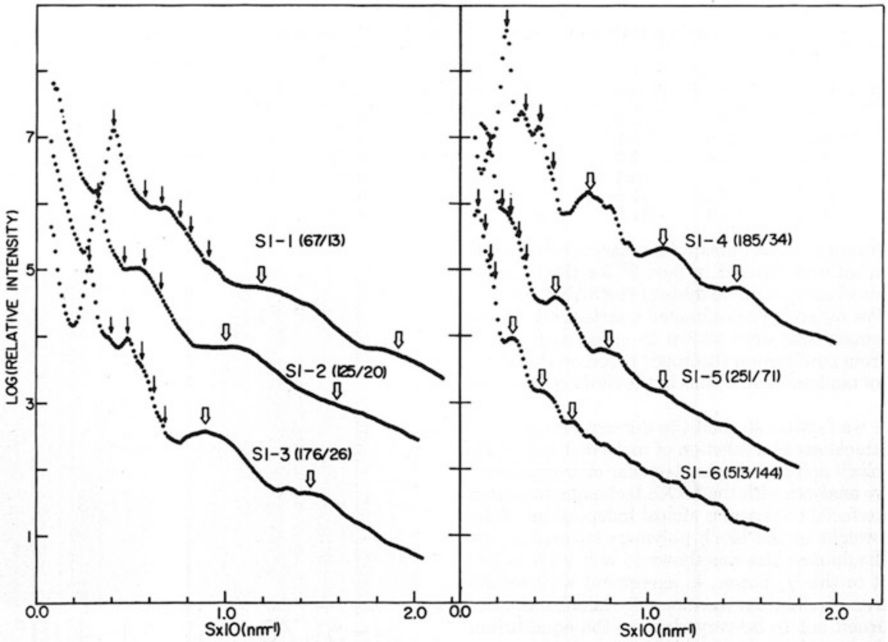


Fig. 1.11 Small angle X-ray scattering of a series of polystyrene-isoprene diblocks (Hashimoto et al. 1980)

(Thomas et al. 1987). The dark circular regions labelled 1, 2, and 3 are polystyrene spheres deposited on the section to confirm the axis and magnitude of tilt between the two projections. Optical diffraction patterns are given in the bottom right inset of each figure.

The importance of projection can be seen here: a hexagonal pattern or an apparent lamellae pattern by itself could also arise from packed cylinders, but tilting would reveal the specimen for what it is.

Graft copolymers can also produce segregated domains, similar in appearance to block copolymers, but less regular (Price et al. 1974).

Periodic structures can also be imaged by phase contrast (defocus) techniques, but these require care as artefacts are easily produced, especially from non-periodic structures, and it has been suggested that some reports concerning polyurethanes have been misinterpreted (Roche and Thomas 1981).

Figure 1.11 shows small angle X-ray scattering from a series of polystyrene-isoprene diblocks (labelling shows PS/PI segment molecular weights × 10^{-4}). Shows peaks both from the lattice arrangement of the PI spheres (simple arrows at lower S) and scattering function of the original spheres (open arrows at higher S). The lower S-values at higher molecular weights derive from the ability of longer Gaussian chains to fit into larger spheres, and from the smaller proportion of chain junctions in a given volume of material.