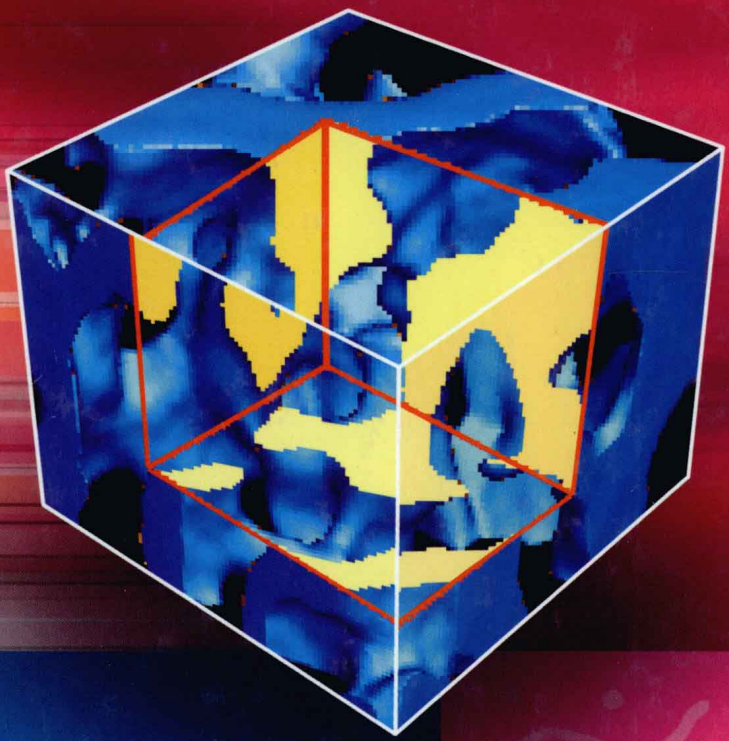
Developments in BLOCK COPOLYMER Science and Technology



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Library of Congress Cataloging-in-Publication Data

Developments in block copolymer science and technology / edited by Ian W. Hamley.
p. cm.
Includes bibliographical references.
ISBN 0–470–84335–7 (Cloth : alk. paper)
1. Block copolymers. I. Hamley, Ian W.
QD382.B5D49 2004
547' .84–dc22

2003016092

British Library Cataloguing in Publication Data

A catalogue record for this book is available from the British Library

ISBN: 0 470 84335 7

Typeset in 10/12pt Times by Kolam Information Services Pvt. Ltd, Pondicherry, India
Printed and bound in Great Britain by Cromwell Press, Trowbridge, Wiltshire
This book is printed on acid-free paper responsibly manufactured from sustainable forestry in which at least two trees are planted for each one used for paper production.

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Preface

Block copolymers are important materials in which the properties of distinct polymer chains are combined or "alloyed". A number of valuable books on block copolymers appeared in the 1980s and 1990s, in particular the two volumes "Developments in Block Copolymers" edited by Goodman [1,2] and my own monograph "The Physics of Block Copolymers" [3]. Recently, Hadjichristidis *et al.* [4] have provided an interesting overview of synthesis, together with physical properties. However, there have recently been significant advances in several aspects of the subject that have not been fully reviewed. For example, thin-film morphology characterization and nanoscience and technology applications are presently attracting a great deal of attention. There have also been major developments in computer modelling of phase behaviour and dynamics. New polymerization methods have been introduced that have led to the emergence of novel products and applications. At a more fundamental level, there has been substantial progress in understanding the crystallization process in block copolymers, and the mechanism of phase transformations in block copolymers in bulk phases. This volume is motivated by a desire to provide up-to-date reviews in these key topics. It is by no means exhaustive, but should be a useful introduction to the recent literature.

I wish to thank the contributors for providing the benefits of their considerable expertise in a timely and professional manner. I am also grateful to Jenny Cossham from Wiley for her help in the production of this volume. Finally, thanks to Valeria Castelletto for all her love, support and companionship.

Ian W. Hamley
Leeds, 2003

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Contents

1 Introduction to Block Copolymers

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1.1 INTRODUCTION

Block copolymers are useful in many applications where a number of different polymers are connected together to yield a material with hybrid properties. For example, thermoplastic elastomers are block copolymers containing a rubbery matrix (polybutadiene or polyisoprene) containing glassy hard domains (often polystyrene). The block copolymer, a kind of polymer alloy, behaves as a rubber at ambient conditions, but can be moulded at high temperatures due to the presence of the glassy domains that act as physical crosslinks. In solution, attachment of a water soluble polymer to an insoluble polymer leads to the formation of micelles in amphiphilic block copolymers. The presence of micelles leads to structural and flow characteristics of the polymer in solution that differ from either parent polymer.

A block copolymer molecule contains two or more polymer chains attached at their ends. Linear block copolymers comprise two or more polymer chains in sequence, whereas a starblock copolymer comprises more than two linear block copolymers attached at a common branch point. Polymers containing at least three homopolymers attached at a common branching point have been termed mixed arm block copolymers, although they can also be viewed as multigraft copolymers.

In the following, block copolymers prepared by controlled polymerization methods only are considered, primarily di- and tri-block copolymers (see Figure 1.1). Multiblock copolymers such as polyurethanes and poly (urethane-ureas) prepared by condensation polymerisation are not discussed. Whilst these materials do exhibit microphase separation, it is only short range in spatial extent due to the high polydispersity of the polymers.

A standard notation for block copolymers is becoming accepted, whereby X-*b*-Y denotes a diblock copolymer of polymer X and polymer Y. However, sometimes the *b* is replaced by the full term *block*, or alternatively is omitted, and the diblock is denoted X-Y.

A number of texts covering general aspects of block copolymer science and engineering appeared in the 1970s and 1980s and these are listed elsewhere [1]. More recently, specialised reviews have appeared on block copolymer melts and

Developments in Block Copolymer Science and Technology. Edited by I. W. Hamley
 ISBN: 0-470-84335-7

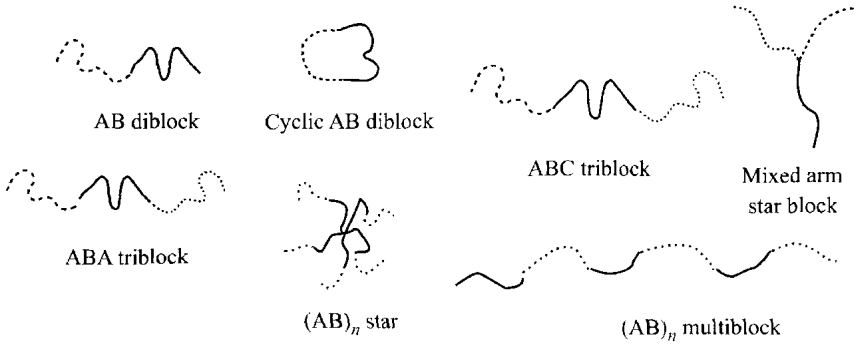

Figure 1.1 Block copolymer architectures.

block copolymer solutions, and these are cited in Sections 1.3 and 1.4 below. The burgeoning interest in block copolymers is illustrated by contributions covering various aspects of the subject in a review journal [2] and in a book [3].

Since the excellent review by Riess *et al.* [4] there have been many advances in the field of block copolymer science and engineering, including new synthesis methods, developments in the understanding of phase behaviour and the investigation of structure and dynamics in thin films. Many of these advances are likely to lead soon to novel applications.

1.2 SYNTHESIS

The main techniques for synthesis of block copolymers in research labs around the world are presently anionic polymerization and controlled radical polymerization methods. The older technique of anionic polymerization is still used widely in the industrial manufacture of block copolymers. Cationic polymerization may be used to polymerize monomers that cannot be polymerized anionically, although it is used for only a limited range of monomers. A summary of block copolymer synthesis techniques has been provided by Hillmyer [5].

1.2.1 ANIONIC POLYMERIZATION

Anionic polymerization is a well-established method for the synthesis of tailored block copolymers. The first anionic polymerizations of block copolymers were conducted as early as 1956 [6]. To prepare well-defined polymers, the technique is demanding, requiring high-purity starting reagents and the use of high-vacuum procedures to prevent accidental termination due to the presence of impurities. In the lab, it is possible to achieve polydispersities $M_w/M_n < 1.05$ via anionic polymerization. The method is also used industrially to prepare

several important classes of block copolymers including SBS-type thermoplastic elastomers (S = polystyrene, B = polybutadiene) and polyoxyethylene-*b*-polyoxypropylene-*b*-polyoxyethylene Pluronic amphiphilic copolymers [3]. The principles of anionic polymerization are discussed in Chapter 2. There are a number of reviews that cover its application to block copolymers [7–11]. Recent advances have mainly been directed towards the synthesis of block copolymers with exotic architectures, such as mixed arm stars [12–14], H-shaped copolymers [12], ring-shaped (cyclic) block copolymers [15], etc. All of these require the careful choice of multifunctional initiators.

1.2.2 LIVING RADICAL POLYMERIZATION

Undoubtedly the main advance in block copolymer synthesis in the last decade has been the development of techniques of living radical polymerization (sometimes termed controlled radical polymerization). The principle of controlled radical polymerization methods is to establish a dynamic equilibrium between a small fraction of growing free radicals and a large majority of dormant species. Generated free radicals propagate and terminate as in conventional radical polymerization, although the presence of only a small fraction of radicals prevents premature termination. Among living polymerization methods, atom-transfer radical polymerization (ATRP) has been used most extensively to synthesize block copolymers. Here, the radicals are generated through a reversible redox process catalysed by a transition metal complex that undergoes a one-electron oxidation with the abstraction of a halogen atom from the dormant species. The ATRP method, and its application to the synthesis of block copolymers, has recently been reviewed [16].

ATRP has been used to prepare AB diblock, ABA triblock and most recently ABC triblock copolymers [17]. To date, the technique has been used to create block copolymers based on polystyrene and various polyacrylates [16]. However, it is possible to synthesize a so-called macroinitiator by other polymerization mechanisms (anionic, cationic, etc.), and use this in the ATRP of vinyl monomers. Examples, such as the anionic polymerization of PEO macroinitiators for ATRP synthesis of PEO/PS block copolymers, are discussed by Matyjaszewski and Xia [16].

1.2.3 OTHER METHODS

Sequential living cationic polymerization is primarily used to prepare block copolymers containing a vinyl ether block, or polyisobutylene [18–20]. It can also be coupled with other techniques [18,20]. However, the range of monomers that may be polymerized by this method is comparatively limited and consequently living cationic polymerization is only used in prescribed circumstances.

Ring-opening metathesis polymerization has also been exploited to build blocks from cyclic olefins, especially polynorbornene [5]. The development of ROMP for block copolymer synthesis has recently been facilitated by the introduction of functional-group-tolerant metathesis catalysts by Grubbs [21].

1.3 BLOCK COPOLYMER MELTS

The interest in the phase behaviour of block copolymer melts stems from microphase separation of polymers that leads to nanoscale-ordered morphologies. This subject has been reviewed extensively [1,22–24]. The identification of the structure of bicontinuous phases has only recently been confirmed, and this together with major advances in the theoretical understanding of block copolymers, means that the most up-to-date reviews should be consulted [1,24]. The dynamics of block copolymer melts, in particular rheological behaviour and studies of chain diffusion via light scattering and NMR techniques have also been the focus of several reviews [1,25,26].

The phase behaviour of block copolymer melts is, to a first approximation, represented in a morphology diagram in terms of χN and f [1]. Here f is the volume fraction of one block and χ is the Flory–Huggins interaction parameter, which is inversely proportional to temperature, which reflects the interaction energy between different segments. The configurational entropy contribution to the Gibbs energy is proportional to N, the degree of polymerization. When the product χN exceeds a critical value, $(\chi N)_{\mathrm{ODT}}$ (ODT = order–disorder transition) the block copolymer microphase separates into a periodically ordered structure, with a lengthscale $\sim 5 - 500\,\mathrm{nm}$. The structure that is formed depends on the copolymer architecture and composition [1]. For diblock copolymers, a lamellar (lam) phase is observed for symmetric diblocks ($f = 0.5$), whereas more asymmetric diblocks form hexagonal-packed cylinder (hex) or body-centred cubic (bcc) spherical structures. A complex bicontinuous cubic gyroid (gyr) (spacegroup $Ia\bar{3}d$) phase has also been identified [27,28] for block copolymers between the lam and hex phases near the ODT, and a hexagonal-perforated layer (hpl) phase has been found to be metastable in this region [29–31]. A useful compilation is available of studies on the morphology of block copolymers of various chemistries [32].

The main techniques for investigating solid block copolymer microstructures are transmission electron microscopy (TEM) and small-angle X-ray or neutron scattering. TEM provides direct images of the structure, albeit over a small area of the sample. Usually samples are stained using the vapours from a solution of a heavy metal acid (OsO_4 or RuO_4) to increase the contrast for electrons between domains [33]. Small-angle scattering probes the structure over the whole sample volume, giving a diffraction pattern. The positions of the reflections in the diffraction pattern can be indexed to identify the symmetry of the phase [1,22]. The preparation method can have a dramatic influence

on the apparent morphology, for example whether solvent casting or melt processing is performed. Numerous cases of mistaken identification of "equilibrium phases" have appeared in the literature, when the phase was simply an artifact. For instance, Lipic *et al.* [34] obtained different morphologies by varying the preparation conditions for a polyolefin diblock examined by them. In other cases, phases such as hexagonal perforated layers have been observed [29], which, although reproducible, have turned out to be only long-lived metastable phases, ultimately transforming to the equilibrium gyroid phase [30,31]. The ODT in block copolymers can be located via a number of methods – from discontinuities in the dynamic shear modulus [35–37] or small-angle scattering peak shape [38,39] or from calorimetry measurements [40].

To establish relationships between different block copolymer phase diagrams and also to facilitate comparison with theory, it is necessary to specify parameters in addition to χN and f. First, asymmetry of the conformation of the copolymer breaks the symmetry of the phase diagram about $f = 0.5$. For AB diblocks, conformational asymmetry is quantified using the "asymmetry parameter" $\varepsilon = (b_A^2/v_A)/(b_B^2/v_B)$ [41,42], where b_J is the segment length for block J and v_J is the segment volume. Composition fluctuations also modify the phase diagram, and this has been accounted for theoretically via the Ginzburg parameter $\bar{N} = Nb^6\rho^2$, where ρ is the number density of chains [43,44]. The extent of segregation of block copolymers depends on the magnitude of χN. For small χN, close to the order–disorder transition (up to $\chi N = 12$ for symmetric diblocks for which $\chi N_{\mathrm{ODT}} = 10.495$), the composition profile (density of either component) is approximately sinusoidal. This is termed the weak-segregation limit. At much larger values of $\chi N (\chi N >\sim 100)$, the components are strongly segregated and each domain is almost pure, with a narrow interphase between them. This is the strong-segregation limit.

The first theories for block copolymers were introduced for the strong-segregation limit (SSL) and the essential physical principles underlying phase behaviour in the SSL were established in the early 1970s [1]. Most notably, Helfand and coworkers [45–47] developed the self-consistent field (SCF) theory, this permitting the calculation of free energies, composition profiles and chain conformations. In the SCF theory, the external mean fields acting on a polymer chain are calculated self-consistently with the composition profile. The theory of Leibler [48] describes block copolymers in the weak-segregation limit. It employs a Landau–Ginzburg approach to analyse the free energy, which is expanded with reference to the average composition profile. The free-energy coefficients are computed within the random-phase approximation. Weak-segregation limit theory can be extended to allow for thermal-composition fluctuations. This changes the mean-field prediction of a second-order phase transition for a symmetric diblock copolymer to a first-order transition. Fredrickson and Helfand [43] studied this effect for block copolymers and showed that composition fluctuations, incorporated via the renormalization method of Brazovskii,

lead to a "finite-size effect", where the phase diagram depends on $\bar{N}$. A powerful new method to solve the self-consistent field equations for block copolymers has been applied by Matsen and coworkers [49–52] to analyse the ordering of many types of block copolymer in bulk and in thin films. The strong- and weak-segregation limits are spanned, as well as the intermediate regime where the other methods do not apply. This implementation of SCF theory predicts phase diagrams, and other quantities such as domain spacings, in good agreement with experiment (see Figure 1.2) and represents an impressive state-of-the-art for modelling the ordering of soft materials. Accurate liquid-state theories have also been used to model block copolymer melts [53,54], although

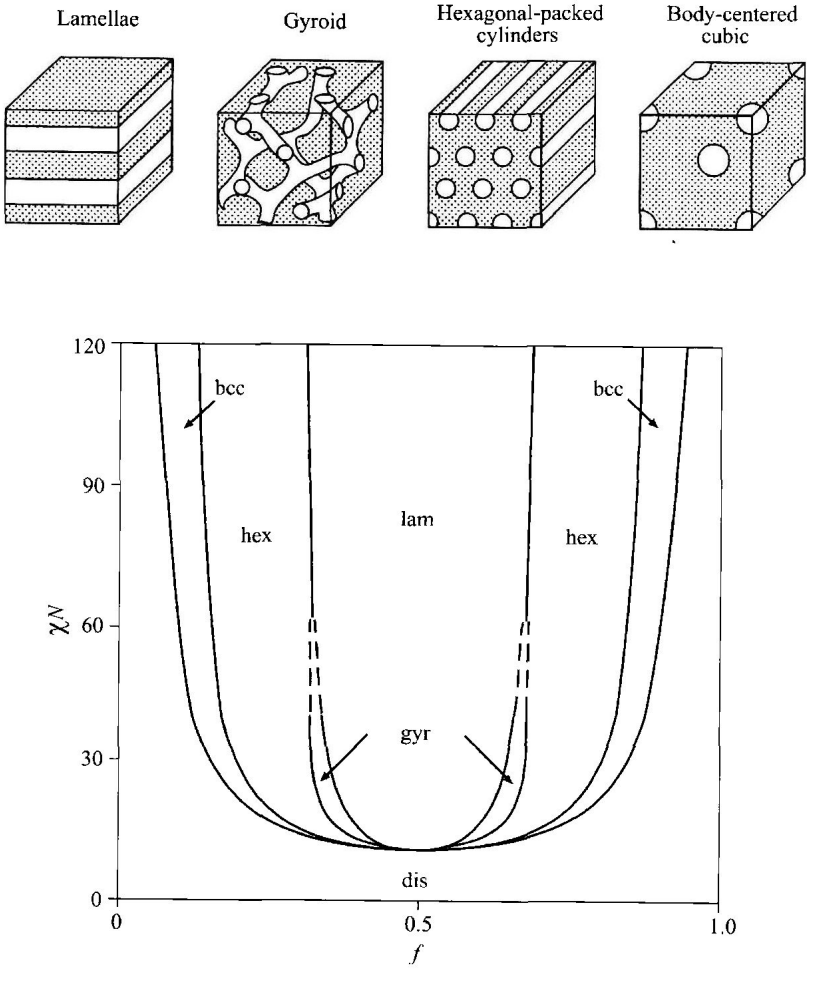

Figure 1.2 Phase diagram for a conformationally symmetric diblock copolymer, calculated using self-consistent mean field theory [49, 51], along with illustrations of the equilibrium morphologies. In the phase diagram, regions of stability of disordered (dis), lamellar (lam), gyroid (gyr), hexagonal (hex) and body-centred cubic (bcc) phases are indicated.

they are hard to implement and consequently the method is often, regrettably, overlooked [1]. Recently, a method has been developed to directly simulate field theories for polymers without introducing approximations such as mean-field approaches, perturbation expansions, etc. [55]. This technique holds much promise for examining the thermodynamics of block copolymers in the limit of low molecular weight where approximate methods such as mean-field theory or renormalization techniques break down.

A phase diagram computed using self-consistent mean field theory [49,51] is shown in Figure 1.2. This shows the generic sequence of phases accessed just below the order–disorder transition temperature for diblock copolymers of different compositions. The features of phase diagrams for particular systems are different in detail, but qualitatively they are similar, and well accounted for by SCF theory.

The phase behaviour of ABC triblocks is much richer [24] than two-component diblocks or triblocks, as expected because multiple interaction parameters (χ_{AB}, χ_{AC} and χ_{BC}) result from the presence of a distinct third block. Summaries of work on ABC triblock morphologies have appeared [1,56]. Because of the large number of possible morphologies, theorists are presently working to predict the phase behaviour of these copolymers using methods that do not require *a priori* knowledge of the space group symmetries of trial structures [57,58].

During processing, block copolymers are subjected to flow. For example, thermoplastic elastomers formed by polystyrene-*b*-polybutadiene-*b*-polystyrene (SBS) triblock copolymers, are moulded by extrusion. This leads to alignment of microphase-separated structures. This was investigated in the early 1970s by Keller and co-workers [22,59] who obtained transmission electron micrographs from highly oriented specimens of Kraton SBS copolymers following extrusion. Examples are included in Figure 1.3. Work on the effect of flow on block copolymer melts has been reviewed [1,25,60,61]. Due to the convenience and well-defined nature of the shear geometry, most model studies have exploited this type of flow. The application of shear leads to orientation of block copolymer microstructures at sufficiently high shear rates and/or strain amplitudes (in the case of oscillatory shear). Depending on shear conditions and temperature, different orientations of a morphology with respect to the shear plane can be accessed. This has been particularly well studied for the lamellar phase where so-called "parallel" (lamellar normal along shear gradient direction) and "perpendicular" (lamellar normal along the neutral direction) orientations have been observed [62]. Distinct orientation states of hexagonal and cubic phases have also been investigated, details being provided elsewhere [61]. The ability to generate distinct macroscopic orientation states of block copolymers by shear is important in future applications of block copolymers, where alignment will be important (reinforced composites, optoelectronic materials and separation media). Shear also influences thermodynamics, since the order–disorder transition shifts upwards on increasing shear rate because the ordered phase is stabilized under shear [63,64].

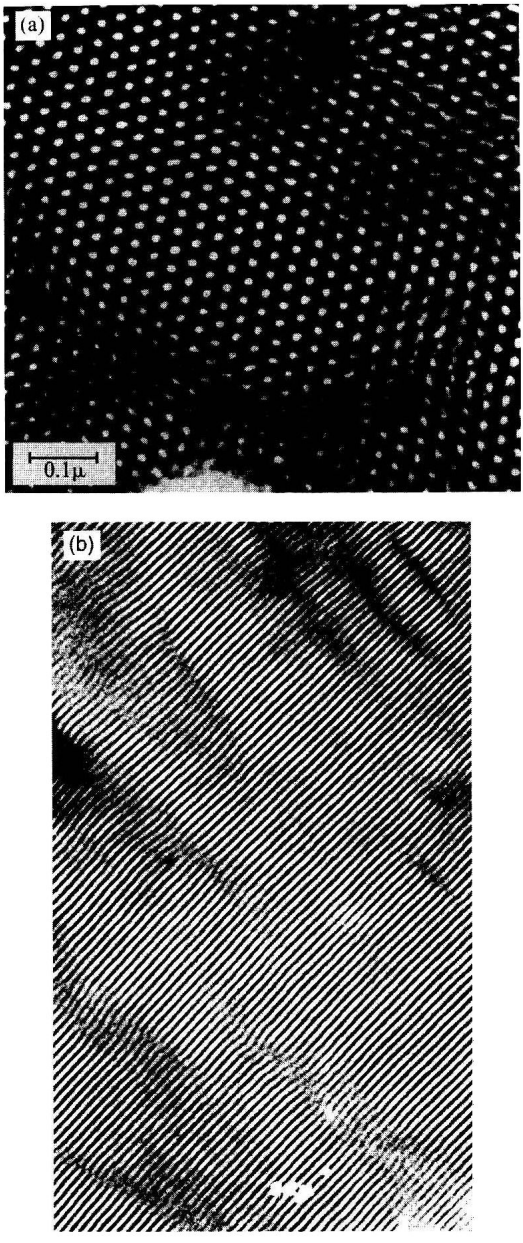

Figure 1.3 TEM micrographs from a hexagonal-packed cylinder structure subjected to flow during high-temperature extrusion. The sample was a PS-PB-PS tribock (Kraton D1102 [209]). (a) Perpendicular to the extrusion direction, (b) a parallel section.