Block Copolymers in Solution: Fundamentals and Applications

IAN HAMLEY
University of Reading, Reading, UK

John Wiley & Sons, Ltd

Block Copolymers in Solution: Fundamentals and Applications

Block Copolymers in Solution: Fundamentals and Applications

IAN HAMLEY
University of Reading, Reading, UK

John Wiley & Sons, Ltd

Telephone (+44) 1243 779777

Email (for orders and customer service enquiries): cs-books@wiley.co.uk
Visit our Home Page on www.wileyeurope.com or www.wiley.com

Other Wiley Editorial Offices

John Wiley & Sons Inc., 111 River Street, Hoboken, NJ 07030, USA

Jossey-Bass, 989 Market Street, San Francisco, CA 94103-1741, USA

Wiley–VCH Verlag GmbH, Boschstr. 12, D-69469 Weinheim, Germany

John Wiley & Sons Australia Ltd, 42, McDougall Street, Milton, Queensland 4064, Australia

John Wiley & Sons (Asia) Pte Ltd, 2 Clementi Loop #02-01, Jin Xing Distripark, Singapore 129809

John Wiley & Sons Canada Ltd, 22 Worcester Road, Etobicoke, Ontario, Canada M9W 1L1

Wiley also publishes its books in a variety of electronic formats. Some content that appears in print may not be availabe in electronic books.

Library of Congress Cataloging-in-Publication Data

Hamley, Ian W.
Block copolymers in solution : fundamentals and applications/Ian Hamley
P. cm.
Includes bibliographical references and index

ISBN-13: 978-0-470-01557-5 (acid-free paper)
ISBN-10: 0-470-01557-8 (acid-free paper)
1. Block copolymers. I. Title
QD382.B5H355 2005
547'.84–dc22 2005005799

British Library Cataloguing in Publication Data

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

ISBN: 0-470-01557-8 (HB); 9-78-0-470-01557-5 (HB)

Typeset in 10/12pt Times by Thomson Press (India) Limited, New Delhi
Printed and bound in Great Britain by TJ International Ltd., Padstow, Cornwall
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.

To Valeria and Lucas

Contents

Preface

I was inspired to write this book by developments in the field of block copolymer self-assembly in solution which have not been discussed and summarized in the form of a single convenient text. Aspects of the subject have been discussed in my previous book,[1] in that by Hadjichristidis *et al.*,[2] and in several chapters of a recent edited text.[3]

Recent advances have been stimulated in part by new synthetic methodologies (living polymerizations in particular) that have enabled the preparation of new materials with novel self-assembling structures, functionality and responsiveness. The present text covers the principles of self-assembly in both dilute and concentrated solution (micellization, mesophase formation, etc.) in Chapters 2 and 3, respectively. Chapter 4 covers polyelectrolyte block copolymers–these materials are just beginning to attract significant attention from researchers and a solid basis for understanding their physical chemistry is emerging, and this is discussed. Chapter 5 discusses adsorption of block copolymers from solution at liquid and solid interfaces. Chapter 6 concludes with a discussion of selected applications, focusing on several important new concepts rather than providing an account of commercial applications, which can be found elsewhere.

I wish to thank several colleagues and collaborators for support and for helpful comments on several chapters: Colin Booth for Chapters 2 and 3, Steve Armes for Chapter 4, Harm-Anton Klok for Chapters 4 and 6. Tom Waigh also provided particularly insightful comments on Chapter 4. As usual I bear full responsibility for any errors and omissions, of which I would be grateful to be informed.

I wish to thank Jenny Cossham for her continued support and attention in editing this book. I am also grateful to the Leverhulme Trust who provided a Leverhulme Research Fellowship which freed up time from some of my usual academic duties, enabling this book to be completed.

REFERENCES

(1) Hamley, I. W. *The Physics of Block Copolymers*. Oxford University Press: Oxford, 1998.
(2) Hadjichristidis, N.; Pispas, S.; Floudas, G. *Block Copolymers. Synthetic Strategies, Physical Properties and Applications*. John Wiley & Sons: New York, 2003.
(3) Hamley, I. W. (Ed.) *Developments in Block Copolymer Science and Technology*. John Wiley & Sons, Ltd: Chichester, 2004.

1 Introduction

This book is concerned with the numerous aspects of the self-assembly of block copolymers in solution, and the diverse applications of this. Block copolymers in the melt, or in blends are not considered, and information on this can be found elsewhere.[1]

An early review of micellization in block copolymers was presented by Tuzar and Kratochvíl,[2] and these authors provided a further review of the literature up to 1992.[3] Micellar properties of block copolymers were reviewed earlier by Price.[4] A discussion of micellization was included in the general reviews on block copolymers by Riess *et al.*[5] and Brown *et al.*[6] Riess has recently published a very nice review specifically dedicated to micellization in block copolymers.[7] Excellent reviews focused on the solution properties of a particular class of copolymer, i.e. copolymers of poly(oxyethylene) with poly(oxypropylene), have been presented by several groups.[8–13] Micellization and micellar association in related poly(oxyethylene)/poly(oxybutylene) copolymers has been summarized by Booth *et al.*[14–16]

The micellar properties of block copolymers in dilute solution, the properties of adsorbed block copolymers and ordered mesophase (lyotropic liquid crystal phase) formation in more concentrated solutions have been comprehensively discussed.[1] Reviews on structure/rheology relationships in block copolymer gels,[17] and on shear-alignment of ordered mesophases[18,19] (the latter review incorporates work on block copolymer melts also) have also been provided.

Liu and Armes[20], Liu *et al.*[21] and Förster[22,23] have reviewed the self-assembly of amphiphilic block copolymers, and the numerous applications of the resulting nanostructures.

Applications of block copolymer surfactants have been the subject of a number of reviews by researchers from Dow in the United States.[24–26] The texts edited by Nace[27] and by Alexandridis and Lindman[28] cover many aspects of the behaviour and properties of PEO-based amphiphilic block copolymers, with several chapters devoted to applications.

A standard notation for block copolymers is becoming accepted whereby, for example, PX-*b*-PY denotes a diblock copolymer of polymer X and polymer Y.[29] This convention is used here. In the case that a specific polymer with defined chain lengths is considered, the molecule is denoted X_m-*b*-Y_n, where m and n are degrees of polymerization. This notation is somewhat more cumbersome than alternatives. For example, Booth and coworkers use single letters to indicate blocks in

Block Copolymers in Solution: Fundamentals and Applications I. W. Hamley