
Block Copolymers in Solution: Fundamentals and Applications

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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 available 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	xi
1. Introduction	1
References	5
2. Neutral Block Copolymers in Dilute Solution	7
2.1 Introduction	7
2.2 Techniques for Studying Micellization	7
2.2.1 Cryo-TEM	7
2.2.2 Differential Scanning Calorimetry	8
2.2.3 Dynamic Light Scattering	8
2.2.4 Ellipsometry	10
2.2.5 Fluorescence Probe Experiments	10
2.2.6 Nuclear Magnetic Resonance	10
2.2.7 Rheology	11
2.2.8 Scanning Probe Microscopy	11
2.2.9 Small-angle X-ray and Neutron Scattering	12
2.2.10 Static Light Scattering	14
2.2.11 Surface Pressure–Area Isotherms	16
2.2.12 Surface Tensiometry	16
2.2.13 Viscometry	17
2.2.14 X-ray and Neutron Reflectivity	17
2.3 Micellization in PEO-based Block Copolymers	18
2.4 Micellization in Styrenic Block Copolymers	20
2.5 Determination of cmc	20
2.6 Thermodynamics of Micellization	22
2.6.1 Chain Length Dependence of Micellization	25
2.6.2 Effect of Architecture	27
2.6.3 Effect of Solvents and Salts on Micellization	32
2.7 Micellization and Micelle Dimensions: Theory and Simulation	33
2.7.1 Scaling Models	33
2.7.2 The Brush Model	37
2.7.3 The Self-consistent Mean Field Theory	40
2.7.4 The Model of Nagarajan and Ganesh	43
2.7.5 Computer Simulations	44

2.7.6 Theory: ABC Triblock Micelles	45
2.8 Micelle Dimensions: Comparison Between Experiment and Theory	47
2.9 Interaction between Micelles	51
2.10 Dynamics of Micellization	52
2.11 Dynamic Modes	56
2.12 Specific Types of Micelles	60
2.12.1 Micelles from Telechelics	60
2.12.2 Micelles from ABC Triblocks	62
2.12.3 Micelles from Rod–Coil Copolymers	66
2.12.4 Cross-linked Micelles	68
2.12.5 Janus Micelles	71
2.12.6 Nonspherical Micelles	71
2.12.7 Micelles Formed due to Specific Interactions	74
2.13 Micellization in Mixed Solvents	75
2.14 Mixed Micelles	75
2.15 Block Copolymer/Surfactant Complexes	76
2.16 Complex Morphologies	79
2.17 Vesicles	83
2.18 Crystallization in Micelles	90
References	91

3. Concentrated Solutions 105

3.1 Understanding Phase Diagrams	105
3.2 Phase Behaviour of PEO-containing Block Copolymers	111
3.3 Gelation	117
3.3.1 Rheology	117
3.3.2 Structure – Packing of Micelles	124
3.3.3 Thermodynamics of Gelation and Micellization in Concentrated Solution	126
3.3.4 Effect of Added Homopolymer, Salt or Surfactant	127
3.3.5 Influence of Architecture	129
3.4 Order–Disorder Phase Transition	132
3.5 Order–Order Phase Transitions	135
3.5.1 Structural Aspects	135
3.5.2 Ordering Kinetics	139
3.6 Domain Spacing Scaling, and Solvent Distribution Profiles	140
3.7 Semidilute Block Copolymer Solution Theory	143
3.8 Theoretical Understanding of Phase Diagrams	146
3.9 Flow Alignment	149
3.9.1 Lamellar Phase	149
3.9.2 Hexagonal Phase	151

3.9.3 Cubic Micellar Phases	152
3.10 Dynamics	159
3.10.1 Dynamic Modes	159
3.10.2 Dynamics of Gelation	160
References	164
4. Polyelectrolyte Block Copolymers	173
4.1 Micellization	173
4.1.1 General Remarks	173
4.1.2 Micellization in Block Copolymers Containing Anionic Blocks	175
4.1.3 Micellization in Block Copolymers Containing Cationic Blocks	179
4.1.4 Micellization of Polyampholyte Block Copolymers	182
4.1.5 Micellization of Polyelectrolyte-containing ABC triblocks	182
4.1.6 Micellization of Block Copolymers Containing Grafted Polyelectrolytes	183
4.1.7 Micellization in Block Copolymers Containing Sulfonated Polyisoprene	183
4.2 Chain Conformation	184
4.3 Theory	188
4.4 Polyion Complexes	195
4.5 Copolymer–Surfactant Complexes	198
4.6 Complexation with other Molecules	199
4.7 Gelation	200
4.8 Hierarchical Order in Peptide Block Copolyelectrolyte Solutions	200
4.8.1 α Helix Structures	202
4.8.2 β Sheet Structures	204
4.8.3 Hydrogels	206
4.8.4 Polypeptide Block Copolymer-based Complexes	207
References	208
5. Adsorption	215
5.1 Introduction	215
5.2 Adsorption at the Air–Water Interface	215
5.2.1 Adsorption of Neutral Block Copolymers	215
5.2.2 Adsorption of Polyelectrolyte Block Copolymers	221
5.3 Adsorption on Solid Substrates	222
5.3.1 Adsorption of Neutral Block Copolymers	222
5.3.2 Adsorption of Polyelectrolyte Block Copolymers	225

5.3.3 Surface Micelles	226
5.4 Surface Forces Experiments	231
5.5 Modelling Adsorption	234
References	236
6. Applications	241
6.1 Surfactancy/Detergency	241
6.2 Solubilization, Emulsification and Stabilization	241
6.2.1 Solubilization	241
6.2.2 Emulsification and Stabilization	245
6.3 Drug Delivery	247
6.4 Biodegradable Block Copolymer Micelles	253
6.5 Thermoresponsive Micellar Systems	254
6.6 Metal-containing Copolymer Micelles and Nanoreactors	255
6.7 Vesicles	261
6.8 Separation Media	268
6.9 Templating	268
6.10 Membranes	274
6.11 Other Applications	275
References	276
Index	285

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.

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- (2) Hadjichristidis, N.; Pispas, S.; Floudas, G. *Block Copolymers. Synthetic Strategies, Physical Properties and Applications*. John Wiley & Sons: New York, 2003.
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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 Armes²⁰, 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 Nace²⁷ and by Alexandridis and Lindman²⁸ 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