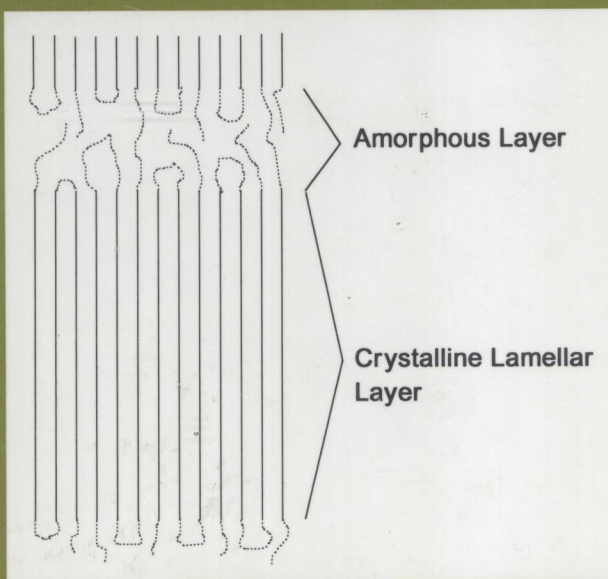


surfactant science series

volume **60**

# NONIONIC SURFACTANTS

Polyoxyalkylene Block Copolymers



edited by  
Vaughn M. Nace

0647  
N813

9860227

# NONIONIC SURFACTANTS

Polyoxyalkylene Block Copolymers

edited by  
Vaughn M. Nace  
*The Dow Chemical Company  
Freeport, Texas*



E9860227

Marcel Dekker, Inc.

New York • Basel • Hong Kong

## Library of Congress Cataloging-in-Publication Data

Nonionic surfactants: polyoxyalkylene block copolymers / edited by  
Vaughn M. Nace.

p. cm. — (Surfactant science series ; v. 60)

Includes index.

ISBN 0-8247-9700-0 (hardcover: alk. paper)

1. Surface active agents. 2. Block copolymers. I. Nace, Vaughn  
Mark. II. Series.

TP994.N66 1996

668'.1—dc20

96-2619

CIP

The publisher offers discounts on this book when ordered in bulk quantities.  
For more information, write to Special Sales/Professional Marketing at the  
address below.

This book is printed on acid-free paper.

Copyright © 1996 by Marcel Dekker, Inc. All Rights Reserved.

Neither this book nor any part may be reproduced or transmitted in any form  
or by any means, electronic or mechanical, including photocopying, microfilm-  
ing, and recording, or by any information storage and retrieval system, without  
permission in writing from the publisher.

Marcel Dekker, Inc.

270 Madison Avenue, New York, New York 10016

Current printing (last digit):

10 9 8 7 6 5 4 3 2 1

PRINTED IN THE UNITED STATES OF AMERICA

# **NONIONIC SURFACTANTS**

## Preface

Polyoxyalkylene block copolymer surfactants are a diverse subset of nonionic surfactants. This diversity results from the numerous structural possibilities available to the oxide chemist during synthesis. This volume focuses mainly on polyoxyalkylene copolymers made from the appropriate sequential block polymerization of ethylene oxide (EO), propylene oxide (PO), and 1,2-butylene oxide (BO). Some discussion of polyoxyalkylene homopolymer precursors of block copolymers is presented, when necessary, to provide clarification or explanation. Because this subject is treated fully in Volume 1 of this series, we have not focused heavily on surfactants made from hetero-polymerized or randomly polymerized oxides. Block copolymers derived from other monomers such as styrenics are not discussed because many tertiary references are already available.

The volume will be useful not only to researchers and application chemists working in the area of polyoxyalkylene surfactants, but also to those who develop closely related materials such as alkyl phenol ethoxylates, fatty alcohol ethoxylates, and other alkoxyated compounds.

Polyoxyalkylene block copolymers used in the urethanes industry are typically trifunctional and higher. Moreover, they are not used as surfactants per se, but as an integral chemical building block of the urethane system. Polymers having hydroxyl functionality greater than two will be discussed only in relation to their potential use as nonionic surfactants or in synthetic procedures.

Polyoxyalkylene copolymers are unique in that several degrees of freedom found in the manufacturing process may be utilized to give molecules that are tailor-made for specific uses. Among these are the variables of initiator type, initiator functionality, oxide species, oxide feed order, and block molecular

weight. With these degrees of synthetic freedom in mind, Chapter 1 provides a thorough discussion of oxide polymerization fundamentals. Much of the information is offered as a framework for real-life synthetic situations, clearly emphasizing the aspect of block copolymer purity in terms of synthetic procedures. Chemical modification of the hydroxyl end group is also discussed.

Chapter 2 covers modern methods for the chemical analysis of polyoxyalkylene block copolymers. A thorough, well-referenced background in block copolymer analysis is presented. Copolymer structural analysis is then discussed in four sections covering general characterization, molecular weight, EO/PO ratio, and unsaturation. Analytical details for measuring copolymer composition as a whole are also given.

Chapter 3 presents an in-depth view of the physical chemical aspects of polyoxyalkylene block copolymers. The dilute aqueous association characteristics of block copolymer surfactants are discussed in terms of critical micelle concentration, critical micelle temperature, micellization thermodynamics, micellar structure, and association number. The effects of block copolymer non-homogeneity and block architecture are also presented in detail. Block copolymer surface activity and solubilization phenomena are fully documented by using extensive tabulated data derived from numerous sources. The unique phase behavior and gelation properties of some polyoxyalkylene block copolymers have been the topics of numerous research manuscripts covering a 20 year period, and accelerating. The last half of Chapter 3 covers these aspects in great detail.

Chapter 4 deals with the properties of polyoxyalkylene block copolymers as related to physical handling and surfactant performance. The properties of crystallinity, melt viscosity, hydrophobe polarity, and thermal stability are discussed. Generalized wetting and foaming data are presented followed by a section giving detailed information on the relative performance of block copolymers based on polyoxypropylene and polyoxybutylene hydrophobes.

Chapter 5 is an up-to-date synopsis of applications for polyoxyalkylene block copolymer surfactants. Numerous examples are included covering the areas of medicine, coal and petroleum, plastics, emulsion polymerization, paper, photography, cleaner systems, personal care, and others.

Toxicological properties of polyoxyalkylene block copolymers are summarized in Chapter 6. Short- and long-term mammalian toxicity information along with metabolic data are provided. Mutagenicity and genotoxicity is discussed in conjunction with the subject of human safety followed by a section on structure-activity relationships.

Chapter 7, the final chapter, but by no means the least important chapter, treats environmental aspects of block copolymers. Biodegradation and aquatic toxicity are important topics for any modern discussion of surfactant materials. The chapter covers a variety of useful subjects including the environmental

distribution of block copolymers, aquatic toxicity, and biodegradability issues including analytical methods, and degradation mechanisms.

I want to thank Dr. Martin J. Schick, who continues to be the driving force and visionary for the Surfactant Science Series. His help in obtaining the best chapter authors for this book was invaluable. I would also like to thank Dr. Irving R. Schmolka for his moral support and for showing his deep understanding of this subject. The teachings of Milton J. Rosen have been invaluable to me and others in the surfactant science field; my sincere gratitude goes to him. A multitude of thanks goes to the individual authors for their time and effort in putting together their respective chapters. Lastly, I would like to thank Richard E. Rozelle of The Dow Chemical Company for his support in the technical production of this work.

*Vaughn M. Nace*

## Contributors

**Robert E. Bailey**<sup>\*</sup> Environmental Toxicology Laboratory, The Dow Chemical Company, Midland, Michigan

**Benjamin Chu** Department of Chemistry, State University of New York at Stony Brook, Stony Brook, New York

**Michael W. Edens** Industrial Polyglycol Research and Development, The Dow Chemical Company, Freeport, Texas

**Henry T. Kalinoski** Analytical Chemistry Section, Unilever Research U.S., Edgewater, New Jersey

**Vaughn M. Nace** Industrial Polyglycol Research and Development, The Dow Chemical Company, Freeport, Texas

**Stephen C. Rodriguez**<sup>†</sup> Department of Toxicology, Stonybrook Laboratories Inc., Princeton, New Jersey

---

*Current affiliations:*

<sup>\*</sup> Bailey Associates, Midland, Michigan

<sup>†</sup> Central Research, Rhône-Poulenc Rorer, Collegeville, Pennsylvania



**Edward J. Singer** Technical Consultant, Environmental Science & Toxicology, Belle Mead, New Jersey

**Robert H. Whitmarsh** Industrial Polyglycol Research and Development, The Dow Chemical Company, Freeport, Texas

**Zukang Zhou** Department of Chemistry, State University of New York at Stony Brook, Stony Brook, New York

## SURFACTANT SCIENCE SERIES

### CONSULTING EDITORS

**MARTIN J. SCHICK**

*Consultant*

*New York, New York*

**FREDERICK M. FOWKES**

*(1915–1990)*

1. Nonionic Surfactants, *edited by Martin J. Schick* (see also Volumes 19, 23, and 60)
2. Solvent Properties of Surfactant Solutions, *edited by Kozo Shinoda* (see Volume 55)
3. Surfactant Biodegradation, *R. D. Swisher* (see Volume 18)
4. Cationic Surfactants, *edited by Eric Jungemann* (see also Volumes 34, 37, and 53)
5. Detergency: Theory and Test Methods (in three parts), *edited by W. G. Cutler and R. C. Davis* (see also Volume 20)
6. Emulsions and Emulsion Technology (in three parts), *edited by Kenneth J. Lissant*
7. Anionic Surfactants (in two parts), *edited by Warner M. Linfield* (see Volume 56)
8. Anionic Surfactants: Chemical Analysis, *edited by John Cross* (out of print)
9. Stabilization of Colloidal Dispersions by Polymer Adsorption, *Tatsuo Sato and Richard Ruch* (out of print)
10. Anionic Surfactants: Biochemistry, Toxicology, Dermatology, *edited by Christian Gloxhuber* (see Volume 43)
11. Anionic Surfactants: Physical Chemistry of Surfactant Action, *edited by E. H. Lucassen-Reynders* (out of print)
12. Amphoteric Surfactants, *edited by B. R. Bluestein and Clifford L. Hilton* (see Volume 59)
13. Demulsification: Industrial Applications, *Kenneth J. Lissant* (out of print)
14. Surfactants in Textile Processing, *Arved Datyner*
15. Electrical Phenomena at Interfaces: Fundamentals, Measurements, and Applications, *edited by Ayao Kitahara and Akira Watanabe*
16. Surfactants in Cosmetics, *edited by Martin M. Rieger* (out of print)
17. Interfacial Phenomena: Equilibrium and Dynamic Effects, *Clarence A. Miller and P. Neogi*
18. Surfactant Biodegradation: Second Edition, Revised and Expanded, *R. D. Swisher*
19. Nonionic Surfactants: Chemical Analysis, *edited by John Cross*
20. Detergency: Theory and Technology, *edited by W. Gale Cutler and Erik Kissa*

21. *Interfacial Phenomena in Apolar Media*, edited by Hans-Friedrich Eicke and Geoffrey D. Parfitt
22. *Surfactant Solutions: New Methods of Investigation*, edited by Raoul Zana
23. *Nonionic Surfactants: Physical Chemistry*, edited by Martin J. Schick
24. *Microemulsion Systems*, edited by Henri L. Rosano and Marc Clausse
25. *Biosurfactants and Biotechnology*, edited by Naim Kosaric, W. L. Cairns, and Neil C. C. Gray
26. *Surfactants in Emerging Technologies*, edited by Milton J. Rosen
27. *Reagents in Mineral Technology*, edited by P. Somasundaran and Brij M. Moudgil
28. *Surfactants in Chemical/Process Engineering*, edited by Darsh T. Wasan, Martin E. Ginn, and Dinesh O. Shah
29. *Thin Liquid Films*, edited by I. B. Ivanov
30. *Microemulsions and Related Systems: Formulation, Solvency, and Physical Properties*, edited by Maurice Bourrel and Robert S. Schechter
31. *Crystallization and Polymorphism of Fats and Fatty Acids*, edited by Nissim Garti and Kiyotaka Sato
32. *Interfacial Phenomena in Coal Technology*, edited by Gregory D. Botsaris and Yuli M. Glazman
33. *Surfactant-Based Separation Processes*, edited by John F. Scamehorn and Jeffrey H. Harwell
34. *Cationic Surfactants: Organic Chemistry*, edited by James M. Richmond
35. *Alkylene Oxides and Their Polymers*, F. E. Bailey, Jr., and Joseph V. Koleske
36. *Interfacial Phenomena in Petroleum Recovery*, edited by Norman R. Morrow
37. *Cationic Surfactants: Physical Chemistry*, edited by Donn N. Rubingh and Paul M. Holland
38. *Kinetics and Catalysis in Microheterogeneous Systems*, edited by M. Grätzel and K. Kalyanasundaram
39. *Interfacial Phenomena in Biological Systems*, edited by Max Bender
40. *Analysis of Surfactants*, Thomas M. Schmitt
41. *Light Scattering by Liquid Surfaces and Complementary Techniques*, edited by Dominique Langevin
42. *Polymeric Surfactants*, Irja Piirma
43. *Anionic Surfactants: Biochemistry, Toxicology, Dermatology. Second Edition, Revised and Expanded*, edited by Christian Gloxhuber and Klaus Künstler
44. *Organized Solutions: Surfactants in Science and Technology*, edited by Stig E. Friberg and Björn Lindman
45. *Defoaming: Theory and Industrial Applications*, edited by P. R. Garrett
46. *Mixed Surfactant Systems*, edited by Keizo Ogino and Masahiko Abe
47. *Coagulation and Flocculation: Theory and Applications*, edited by Bohuslav Dobiáš
48. *Biosurfactants: Production • Properties • Applications*, edited by Naim Kosaric
49. *Wettability*, edited by John C. Berg
50. *Fluorinated Surfactants: Synthesis • Properties • Applications*, Erik Kissa
51. *Surface and Colloid Chemistry in Advanced Ceramics Processing*, edited by Robert J. Pugh and Lennart Bergström

52. Technological Applications of Dispersions, *edited by Robert B. McKay*
53. Cationic Surfactants: Analytical and Biological Evaluation, *edited by John Cross and Edward J. Singer*
54. Surfactants in Agrochemicals, *Tharwat F. Tadros*
55. Solubilization in Surfactant Aggregates, *edited by Sherril D. Christian and John F. Scamehorn*
56. Anionic Surfactants: Organic Chemistry, *edited by Helmut W. Stache*
57. Foams: Theory, Measurements, and Applications, *edited by Robert K. Prud'homme and Saad A. Khan*
58. The Preparation of Dispersions in Liquids, *H. N. Stein*
59. Amphoteric Surfactants: Second Edition, *edited by Eric G. Lomax*
60. Nonionic Surfactants: Polyoxyalkylene Block Copolymers, *edited by Vaughn M. Nace*
61. Emulsions and Emulsion Stability, *edited by Johan Sjöblom*

#### **ADDITIONAL VOLUMES IN PREPARATION**

Applied Surface Thermodynamics, *edited by A. W. Neumann and Jan K. Spelt*

Vesicles, *edited by Morton Rosoff*

Liquid Detergents, *edited by Kuo-Yann Lai*

# Contents

*Preface* iii

*Contributors* ix

1. Synthesis and Chemical Modification of Polyoxyalkylene Block Copolymers 1  
*Robert H. Whitmarsh*
2. Chemical Analysis of Polyoxyalkylene Block Copolymers 31  
*Henry T. Kalinoski*
3. Physical Chemistry of Polyoxyalkylene Block Copolymer Surfactants 67  
*Benjamin Chu and Zukang Zhou*
4. Properties of Polyoxyalkylene Block Copolymers 145  
*Vaughn M. Nace*
5. Applications of Polyoxyalkylene Block Copolymer Surfactants 185  
*Michael W. Edens*
6. Toxicology of Polyoxyalkylene Block Copolymers 211  
*Stephen C. Rodriguez and Edward J. Singer*
7. Biological Activity of Polyoxyalkylene Block Copolymers in the Environment 243  
*Robert E. Bailey*

*Index* 259

# 1

## Synthesis and Chemical Modification of Polyoxyalkylene Block Copolymers

**ROBERT H. WHITMARSH** Industrial Polyglycol Research and Development, The Dow Chemical Company, Freeport, Texas

I.	Polyether Overview	2
A.	General chemistry	2
B.	Molecular weight (block size) considerations	4
C.	Safety considerations	6
II.	Preparation and Characterization of Block Copolymers	7
A.	Polymer initiators	7
B.	Base catalyst	7
C.	Base neutralization	8
D.	Polyether structural considerations	9
E.	Planning the synthesis	11
F.	Polymer characterization	12
III.	Synthetic Challenges	13
A.	Deviations from Flory's first and second assumptions	14
B.	Deviations from Flory's third assumption	16
C.	Other common synthetic problems	21
IV.	Modification of Polyoxyalkylene Block Copolymers	22
A.	Modification of the hydroxyl group	22
B.	Modification of the polyether backbone	25
	References	25

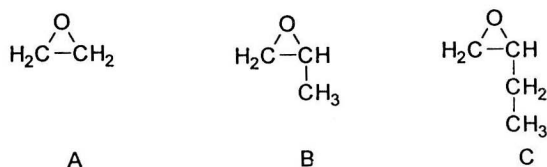
## I. POLYETHER OVERVIEW

### A. General Chemistry

Polyethers are those polymers containing ether (C-O-C) linkages in the chain backbone. Such polymers are quite numerous. They are derived from a wide variety of monomers, by many different synthetic routes. Polyethers find utility in diverse applications either directly or as chemical intermediates [1]. Of necessity this chapter deals with a limited subset of the total polyether realm. Only those polyethers derived from oxirane (also referred to as ethylene oxide and EO), methyloxirane (propylene oxide and PO), and ethyloxirane (1,2-butylene oxide and BO) will be discussed. Structures of these monomers are shown in Fig. 1. As a class these monomers are called oxiranes, alkylene oxides, AOs, or simply oxides.

While much of what will be said applies to all polyethers, the emphasis of this chapter follows the surfactant theme of the book and deals mainly with the synthesis and, to a lesser degree, the modification of block copolymers. Although many different catalyst systems are used for oxide polymerization [2], only the base-catalyzed mechanism is discussed here. The decision to focus only on preparations using base catalysis is appropriate, as strong base is the catalyst system used for most polyoxyalkylene block copolymers offered as surfactants by industry today [3,4]. Other catalysts used today cover a range of compositions including Lewis acids [5–7], metal coordination catalysts [8–10], and metal porphyrin [11–13]. Some of these catalyst systems readily provide stereoregular polyalkylene glycols of PO and BO [14,15]. Base catalyst is able to do so only when pure *l* or *d* oxide isomers are used [16]. While this is an interesting area, no more will be said about stereoregular polyalkylene glycols in this chapter.

Various drawbacks are found in every catalyst system used to date. The reader is encouraged to consider alternate synthetic methods which overcome the problems associated not only with base catalyst discussed below but also



**FIG. 1** Oxiranes of interest. A) Ethylene oxide. B) Propylene oxide. C) 1,2-Butylene oxide.

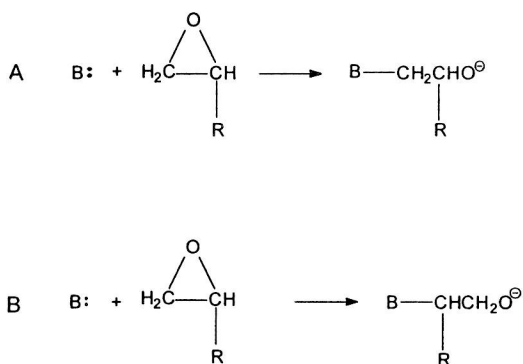
to become familiar with the other systems and the problems associated with each of them.

The base-catalyzed polymerization of alkylene oxides has been known for over a century [17,18]. Industrial applications emerged in the late 1940s [19,20]. Although this chapter is not intended to be all inclusive, it is the author's wish that it be of benefit to surfactant scientists. For those workers who are now discovering the many uses of block copolymers as surfactants the chapter will serve as an introduction to the fundamental chemistry of alkylene oxide polymers. Appreciation of the many examples of how synthesis can go awry will help all workers. Remembering these anomalies will help to explain erratic results from the measurement of surfactant behavior.

Oxiranes are heterocyclic compounds consisting of two carbon and one oxygen atoms in the ring. All such rings are readily opened by a number of reagents. However, many highly substituted oxiranes do not undergo polymerization or do so only with difficulty. At the other extreme EO, PO, and BO polymerize readily with either acid or base catalysis. Commercial polyethers of low molecular weight (less than 20,000 daltons), narrow molecular weight dispersity, and based on these three oxides are prepared using strong base to facilitate the reaction. Base-catalyzed polymerization of alkylene oxides involves nucleophilic attack of an initiator molecule on one carbon of the ring resulting in hetero-bond cleavage. This bond cleavage generates an alkoxide anion. Itself an excellent nucleophile, the alkoxide anion reacts with another oxide molecule, thus propagating polyether chain growth. This is a second-order nucleophilic replacement ( $S_N2$ ) reaction [21]. The substitution reaction is useful for polymerization as the leaving group is not completely released from the molecule. In this way the oxiranes are bifunctional. Figure 2 depicts this propagation reaction; the formation of secondary hydroxyl groups (Reaction A) is greatly favored over primary hydroxyl groups (Reaction B) when propylene oxide and butylene oxide are polymerized under basic conditions [22]. This has been well known for many years. The implications of this selectivity will be discussed further below.

When low molecular weights are involved, this system appears to be a living polymerization [23]. This pseudoliving process allows ready preparation of block copolymers. This is accomplished by reacting different monomers sequentially. Discrete blocks are formed when the concentration of the first oxide is reduced to essentially zero before the introduction of the second oxide. A transition zone containing both monomer units results when the second oxide is introduced before the first has completely reacted. Polyethers with random distributions of monomer units are made by adding different oxides together [24]. Deviation from a true living polymerization is discussed later in the chapter.





**FIG. 2** Polymerization by  $\text{S}_{\text{N}}2$  propagation step.  $\text{R} = \text{H}$ ,  $\text{Me}$ , or  $\text{Et}$ . Polymerizing ethylene oxide,  $\text{R} = \text{H}$ , reactions A and B are identical. With PO and BO, the reaction forming a secondary hydroxyl group (Reaction A) is greatly favored over formation of a primary hydroxy group (Reaction B). Secondary to primary ratio exceeds ten to one. *Source:* from [22].

Polyoxyalkylene block copolymers are efficient surfactants. In these materials EO block(s) provide hydrophilicity and PO (or BO) block(s) the hydrophobicity necessary for surfactancy [25,26].

## B. Molecular Weight (Block Size) Considerations

Polymerization of oxiranes under basic conditions does not proceed indefinitely. Molecular weights of polyethers prepared with a strong base catalyst might approach 20,000 daltons if a molecule with multiple nucleophilic sites is used as the initiating species. With a single site, however, the molecular weight will seldom exceed 5,000 daltons [27,28]. This molecular weight limit is imposed chemically by extraneous introduction of molecules which initiate growth of new polymer chains [29]. From a practical standpoint, molecular weights for industrial processes are limited by increasingly smaller polymerization rates due to a decrease in catalyst concentration as the polymerization proceeds.

Molecular weight distributions in polyethers are generally very narrow. Polydispersities of 1.05 to 1.15 are typical for polyethylene oxides [21] and slightly wider for polypropylene and polybutylene oxides [30]. Narrow dispersity results from three important characteristics of the reacting system:

- all molecules have an equal opportunity to react with monomer,
- reaction rates of addition are equal regardless of molecular weight,