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Fluorinated Ionomers

Second Edition

Walther Grot

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Second edition

Walther Grot
C. G. Processing, Inc.,
Chadds Ford, Pennsylvania

ELSEVIER

AMSTERDAM • BOSTON • HEIDELBERG • LONDON
NEW YORK • OXFORD PARIS • SAN DIEGO
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William Andrew is an imprint of Elsevier

William Andrew is an imprint of Elsevier
The Boulevard, Langford Lane, Kidlington, Oxford, OX5 1GB, UK
225 Wyman Street, Waltham, MA 02451, USA

First edition 2008
Second edition 2011

British Library Cataloguing in Publication Data

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

Library of Congress Control Number: 2011929155

ISBN: 978-1-4377-4457-6

For information on all William Andrew publications visit our website at www.elsevierdirect.com

Printed and bound in the United States

11 12 13 14 10 9 8 7 6 5 4 3 2 1

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Series Editor: Sina Ebnesajjad, PhD
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Notice

PDL Fluorocarbon Series Editor's Preface

The original idea for the Fluorocarbon Series was conceived in the mid-1990s. Two important rationales required the development of the collection. First, there were no definitive sources for the study of fluorinated polymers, particularly the commercial products. A researcher seeking the properties and characteristics of fluorinated plastics did not have a single source to use as a reference. Information available from commercial manufacturers of polymers had long been the source of choice. Second, waves of the post-war generation (a.k.a. Baby Boomers) were beginning to retire, thus eroding the available knowledge base in the industry and academia.

The scope of the series has been expanded over time to incorporate other important fluorinated materials. Selection of the topics of the books has been based on the importance of practical applications. Inevitably, a number of fluorinated compounds, important in their own right, have been left out of the series. In each case, the size of its audience has been found simply too small to meet the economic hurdles of publishing.

The first two books of the series cover commercial fluoropolymers (ethylenic); the third book is focused on their applications in the chemical processing industries. The fourth book covers fluoroelastomers, the fifth fluorinated coatings and finishes, and the sixth book is about fluorinated ionomers, such as Nafion®. The seventh handbook represents an extension of the scope of the series to nonpolymeric materials. It addresses the preparation, properties, and uses of fluorinated chemicals as refrigerants, fire extinguishers, blowing agents, and cleaning gases. A full list of the books in the PDL Fluorocarbon Series appears at the back of this book.

The authors of the handbooks are leaders in their fields who have devoted their professional careers to acquiring expertise. Each book is a product of decades of each author's experience and research into the available body of knowledge. Our hope is that these efforts will meet the needs of the people who work with fluorinated polymers and chemicals. Future revisions are planned to keep this series abreast of progress in the field.

Sina Ebnesajjad

Preface

Fluorinated ionomer polymers are the lesser-known materials, even though they have important industrial applications, particularly in the field of industrial electrochemistry. One of the most important contributions of this polymer to mankind is that it allows elimination of mercury in the production of chlorine and sodium hydroxide, together with a substantial reduction of the electrical energy used in this process. The resulting reduction of the overall worldwide electric energy consumption, both industrial and domestic, is estimated to be almost 1%.

This book covers partially fluorinated and perfluorinated polymers containing sufficient ionic groups to dominate the transport properties of the polymer. The emphasis of this book is on the practical aspects of working with fluorinated ionomers. It is intended to help scientists and engineers in the use of these products, and in the development of new applications and compositions.

The extensive coverage given to perfluorinated ionomers is intentional, because of the practical importance of this group of polymers. Within this group, the emphasis on Nafion® (a trademark of DuPont Company) is not intentional, but is, rather, due to the extensive coverage that this polymer has received in the literature.

Chapters 1 through 4 present the history, manufacturing and properties of perfluorinated ionomers. Even though Chapters 5 and 6 focus on the applications, the latter is devoted to fuel cell and battery applications of these polymers. Chapters 7 and 8 describe the economics and available commercial membranes of fluorinated ionomers. Chapter 9 provides a list of experimental methods used to characterize perfluorinated ionomers. Chapters 10 through 13 discuss heat sealing and repair, handling and storage, toxicology and safety, and suppliers and resources topics. Finally, a series of appendices, information on suppliers and resources, a glossary of terms, and some useful Web sites are provided.

None of the views or information presented in this book reflects the opinions of any of the companies or individuals that have contributed to the book. If there are errors, they are oversights on the part of the author. A note to the publisher indicating the specific error, for the purpose of correcting future editions, would be much appreciated.

Acknowledgements

I would like to acknowledge the contributions made by many individuals in industry and academia, in particular my coworkers at DuPont, foremost Dr. Frank Gresham, who first conceived the idea of introducing sulfonic acid groups into polytetrafluoroethylene. The discovery of Nafion® was made possible by a corporate culture of innovation for its own sake, not driven by the needs of the market. When the potential for the two major applications (membranes for chlor-alkali cells and fuel cells) were recognized in the mid-1960s, the development was pushed ahead even though the economics of these applications did not look attractive at that time.

Special thanks are due to many companies that have contributed data and information to this book. Citation has been made where the material appears in the text.

My special thanks also to the Krupp Uhde for the many excellent pictures and diagrams they made available for this book.

This is the first book I have written, and it would not have been possible without the loving care of my wife Carla during my recovery from a serious operation and the encouragement and help of my editor and friend Dr. Sina Ebnesajjad.

Contents

1 Introduction

Fluorinated ionomers, particularly the perfluorinated ionomers developed in the 1960s, have revolutionized the chlor-alkali industry. In this process, the use of hazardous materials such as mercury and asbestos has been eliminated; and the economics, particularly in regard to reduced energy consumption, has substantially improved. This application has now matured to such an extent that the complete replacement of the two older technologies is only a question of time.

More recently, a new application has emerged in the field of fuel cells. This development is still in flux and is the subject of considerable research in both industry and government institutions. It appears that the full potential of this application is yet to be realized.

The combination of hydrophilic and hydrophobic groups in the same polymer molecule of polymeric fluorinated ionomers results in unique properties and morphologies. This process has attracted the attention of industry, researchers, and theoreticians. However, many questions regarding the inner workings of this material remain still unanswered.

1.1 Polymers

Both partially fluorinated and perfluorinated polymers, containing sufficient ionic groups to dominate the transport properties of the polymer, have been described in this book. Ionic groups may include sulfonic and carboxylic groups as well as sulfonamides and sulfonimides. Due to their importance in the synthesis and fabrication of these ionomers, precursor polymers, containing sulfonyl fluoride or carboxylic ester groups are also discussed. However, it should be emphasized that these precursor polymers are not ionomers, and that they have properties which are quite different from those of the corresponding ionomers.

The synthesis of a perfluorinated ionomer containing phosphonic acid groups has been discussed in detail in [1,2]. Perfluorinated ionomers containing sulfonyl imide functional groups have also received some attention [3].

Within this broad scope, perfluorinated ionomers containing sulfonic or carboxylic functional groups have been covered most extensively due to their many commercial uses. Within this narrower group, the emphasis has been placed on Nafion®, which has been available for about ten years

Fluorinated Ionomers. DOI: 10.1016/B978-1-4377-4457-6.10001-9

longer than any of the other competitive materials in its class. DuPont has made both information and samples of Nafion® and its precursor polymer readily available to research groups and commercial users, which has resulted in extensive coverage of Nafion® in the literature.

More recently, Solvay-Solexis and Minnesota Mining and Manufacturing (3M) have published information about their perfluorinated ionomers, based on monomers of molecular weight 280 and 380 respectively. These polymers differ from Nafion® in that they lack the second ether linkage in the side chain (see Chapter 3). While this structure offers the promise of inherently superior properties it remains to be seen whether the control of important polymerization parameters, such as molecular weight (MW) and its distribution, will allow the realization of this promise. Another consideration is the cost of the manufacturing of the new monomers.

1.2 Physical Shapes

Most fluorinated ionomers are sold as flat sheets and films, such as extruded or solution cast films, or as composite membranes containing fabric reinforcement, which is added to one or more layers of the ionomer. Extruded capillary tubing is also available. Smaller quantities are sold in the form of pellets for applications such as catalysts or for conversion to liquid compositions.

In Chapter 3, monomer synthesis, copolymerization, fabrication, including lamination to a reinforcement, and finishing are described in enough detail to allow the manufacture of these products on a laboratory scale. In Chapter 9, test procedures are provided to determine the properties of both the precursor form as well as the final ionomer. Most important among these properties are equivalent weight (EW) and melt flow (MF). Chapter 3 (Section 3.3) then gives the procedures to adjust these parameters during the copolymerization. A laboratory chlor-alkali cell is described in a way that will allow testing in its most important application, particularly in direct comparison with commercially available membrane types.

The end-use properties as well as the morphology and structure of these products are discussed in Chapter 4.

Chapter 5 deals with the commercial applications. This includes the discussion of chlor-alkali electrolysis, which is the production of chlorine and sodium hydroxide through the electrolysis of brine. This process is still by far the largest and most important application for these ionomers. The major manufacturers have introduced new and improved membranes, known as high performance membranes, which will be covered in Chapter 7. Chapter 8 will discuss how the replacement of the two older chlor-alkali technology by membrane technology is continuing.

In Chapter 6 a section on redox batteries has been added. These are rechargeable batteries, in which the energy storage occurs in liquid electrolytes outside of the cell. Large quantities of energy can then be stored by providing large storage tanks for the electrolytes. This type of large scale energy storage can be used in conjunction with renewable energy sources, such as wind and solar energy, which may not be available at the time of need.

References

[1] M. Kato, K. Akiyama, M. Yamabe, Reps. Res. Lab., Asahi Glass Co. Ltd. 33 (2) (1983) 135.
[2] S. Kotov, S. Pedersen, Z. Qiu, D. Burton, J. Fluorine Chem. 82 (1997) 13–19.
[3] B. Thomas, G. Shafer, J. Ma, M. Tu, D. DesMarteau, J. Fluorine Chem. 125 (8) (2004) 1231–1240.