

Volume 2

Handbook of Engineering and Specialty Thermoplastics

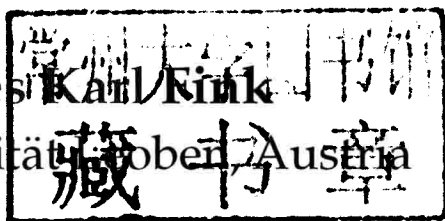
Water Soluble Polymers

Johannes Karl Fink

Handbook of Engineering and Speciality Thermoplastics

Volume 2
Water Soluble Polymers

Johannes Karl Fink
Montanuniversität Leoben, Austria



Scrivener

 **WILEY**

Copyright © 2011 by Scrivener Publishing LLC. All rights reserved.

Co-published by John Wiley & Sons, Inc. Hoboken, New Jersey, and Scrivener Publishing LLC, Salem, Massachusetts.

Published simultaneously in Canada.

No part of this publication may be reproduced, stored in a retrieval system, or transmitted in any form or by any means, electronic, mechanical, photocopying, recording, scanning, or otherwise, except as permitted under Section 107 or 108 of the 1976 United States Copyright Act, without either the prior written permission of the Publisher, or authorization through payment of the appropriate per-copy fee to the Copyright Clearance Center, Inc., 222 Rosewood Drive, Danvers, MA 01923, (978) 750-8400, fax (978) 750-4470, or on the web at www.copyright.com. Requests to the Publisher for permission should be addressed to the Permissions Department, John Wiley & Sons, Inc., 111 River Street, Hoboken, NJ 07030, (201) 748-6011, fax (201) 748-6008, or online at <http://www.wiley.com/go/permission>.

Limit of Liability/Disclaimer of Warranty: While the publisher and author have used their best efforts in preparing this book, they make no representations or warranties with respect to the accuracy or completeness of the contents of this book and specifically disclaim any implied warranties of merchantability or fitness for a particular purpose. No warranty may be created or extended by sales representatives or written sales materials. The advice and strategies contained herein may not be suitable for your situation. You should consult with a professional where appropriate. Neither the publisher nor author shall be liable for any loss of profit or any other commercial damages, including but not limited to special, incidental, consequential, or other damages.

For general information on our other products and services or for technical support, please contact our Customer Care Department within the United States at (800) 762-2974, outside the United States at (317) 572-3993 or fax (317) 572-4002.

Wiley also publishes its books in a variety of electronic formats. Some content that appears in print may not be available in electronic formats. For more information about Wiley products, visit our web site at www.wiley.com.

For more information about Scrivener products please visit www.scrivenerpublishing.com.

Cover designed by Russell Richardson.

Library of Congress Cataloging-in-Publication Data:

ISBN 978-1-118-06275-3

Printed in the United States of America

10 9 8 7 6 5 4 3 2 1

Handbook of Engineering and Speciality Thermoplastics

Scrivener Publishing
3 Winter Street, Suite 3
Salem, MA 01970

Scrivener Publishing Collections Editors

James E. R. Couper	Richard Erdlac
Rafiq Islam	Pradip Khaladkar
Norman Lieberman	Peter Martin
W. Kent Muhlbauer	Andrew Y. C. Nee
S. A. Sherif	James G. Speight

Publishers at Scrivener

Martin Scrivener (martin@scrivenerpublishing.com)
Phillip Carmical (pcarmical@scrivenerpublishing.com)

Preface

This book focuses on water soluble polymers. The text is arranged according to the chemical constitution of polymers and reviews the developments that have taken place in the last decade.

Most chapters follow the same template. A brief introduction to the polymer type is given and previous monographs and reviews dealing with the topic are listed for quick reference. The text continues with monomers, polymerization and fabrication techniques, and discusses aspects of application as well. Following this, suppliers and commercial grades are presented.

How to Use this Book

Utmost care has been taken to present reliable data. Because of the vast variety of material presented here, however, the text cannot be complete in all relevant aspects, and it is recommended to the reader to study the original literature for complete information.

The reader should be aware that in case of patent literature mostly US patents have been cited if available, but not the corresponding equivalent patents in other countries. For this reason, the author cannot assume responsibility for the completeness and validity of, nor for the consequences of, the use of the material presented here. Every attempt has been made to identify trademarks; however, there were some that the author was unable to locate.

Index

There are four indices: an index of trademarks, an index of acronyms, an index of chemicals, and a general index.

In the index of chemicals, compounds that occur extensively, e.g., "acetone", are not included at every occurrence, but rather when they appear in an important context.

Acknowledgements

I am indebted to our university librarians, Dr. Christian Hasenhüttl, Dr. Johann Delanoy, Franz Jurek, Margit Keshmiri, Dolores Knabl, Friedrich Scheer, Christian Slamenik, and Renate Tschabuschnig for support in literature acquisition. I also want to express my gratitude to all the scientists who have carefully published their results concerning the topics dealt with here. This book could not have been otherwise compiled.

Last, but not least, I want to thank the publisher, Martin Scrivener, for his abiding interest and help in the preparation of the text.

Johannes Fink
20th January 2011

Contents

Preface	v
1 Poly(ethylene oxide)	1
1.1 Monomers	1
1.2 Polymerization and Fabrication	2
1.2.1 Functionalization	3
1.2.2 Extrusion	6
1.3 Properties	8
1.4 Special Additives	8
1.5 Applications	9
1.5.1 Textile Impregnation	10
1.5.2 Laundry Detergents	11
1.5.3 Ink Jet Printing Media	12
1.5.4 Flocculation and Coagulation	13
1.5.5 Superabsorbents	14
1.5.6 Food Additive	15
1.5.7 Medical Applications	17
1.6 Suppliers and Commercial Grades	27
1.7 Environmental Impact and Recycling	28
Tradenames	28
References	32
2 Poly(vinyl alcohol)	39
2.1 Monomers	39
2.2 Polymerization and Fabrication	39
2.2.1 Hydrogels	42
2.3 Properties	47
2.3.1 Swelling of Hydrogels	48
2.4 Applications	49
2.4.1 Papermaking	49

2.4.2	Textile Applications	52
2.4.3	Adhesive Applications	53
2.4.4	Corrosion Inhibition	54
2.4.5	Membranes	54
2.4.6	Medical Applications	54
2.5	Suppliers and Commercial Grades	60
2.6	Safety	61
2.7	Environmental Impact and Recycling	61
	Tradenames	61
	References	63
3	Polysaccharides	69
3.1	Polymers	69
3.2	Starch	70
3.2.1	Modified Starch Types	71
3.2.2	Uses of Starch Compositions	72
3.3	Chitosan	76
3.3.1	Nanoparticles	78
3.3.2	Deodorizing Preparations	79
3.3.3	Contact Lens Solutions	79
3.3.4	Intranasal Protein Drug Delivery	80
3.4	Carboxymethyl cellulose	80
3.4.1	Thickeners	83
3.4.2	Superabsorbent Polymers	84
3.4.3	Papermaking	85
3.4.4	Textile Printing	85
3.4.5	Laundry Compositions	86
3.4.6	Shaped Activated Carbon	86
3.4.7	Cosmetics and Medical	87
3.4.8	Enzyme Activity	89
3.5	Guar	89
3.5.1	Phase Separated Solutions	89
3.5.2	Fracturing Fluids	90
3.6	Carrageenan	92
3.6.1	Medical Applications	93
3.6.2	Other Applications	96
3.7	Suppliers and Commercial Grades	97
	Tradenames	99

References	102
4 Poly((meth)acrylic acid)	109
4.1 Monomers	109
4.1.1 Acrylic acid	109
4.1.2 Methacrylic acid	113
4.2 Polymerization and Fabrication	114
4.2.1 Copolymers	114
4.2.2 Hydrolysis of Poly(acrylamide)	118
4.2.3 Slightly Crosslinked Polymers	118
4.3 Properties	119
4.4 Applications	119
4.4.1 Superabsorbent Polymers	119
4.4.2 Viscosifier for Aqueous Compositions	120
4.4.3 Laundry Detergents	121
4.4.4 Emulsifier Compositions	122
4.4.5 Pulps	122
4.4.6 Surface Coating	124
4.4.7 Polishing Integrated Circuits	125
4.4.8 Anti Reflective Coatings in Semiconductor Technology	126
4.4.9 Crosslinked Cellulose	126
4.4.10 Teeth Bleaching Gel	128
4.4.11 Oil Field Applications	132
4.5 Suppliers and Commercial Grades	135
Tradenames	136
References	137
5 Poly(acrylamide)	141
5.1 Monomers	141
5.2 Polymerization and Fabrication	141
5.3 Properties	143
5.3.1 Mechanical Properties	143
5.3.2 Acoustic Properties	144
5.3.3 Thermal Properties	144
5.4 Special Additives	144
5.5 Applications	145
5.5.1 Membranes	145
5.5.2 Sensors	146

5.5.3	Flocculants	146
5.5.4	Hydrogels	147
5.5.5	Agriculture	147
5.5.6	Remediation of Acid Spills	148
5.5.7	Concrete Compositions	149
5.5.8	Paper Additives	149
5.5.9	Oil Field Applications	150
5.5.10	Protein Analysis	154
5.6	Suppliers and Commercial Grades	155
5.7	Safety	156
5.8	Environmental Impact and Recycling	156
	Tradenames	157
	References	159
6	Poly(vinylamine)	165
6.1	Monomers	165
6.2	Polymerization and Fabrication	166
6.2.1	Poly(<i>N</i> -vinylamine)	166
6.2.2	Popcorn Polymers	168
6.2.3	Carbamates	169
6.2.4	Phosphonomethylated Poly(<i>N</i> -vinylamine)s	169
6.3	Applications	170
6.3.1	Flocculants and Demulsifiers	170
6.3.2	Anti-scaling Agents	173
6.3.3	Water Absorbent Materials	174
6.3.4	Papermaking	177
6.3.5	Tanning Materials	179
6.3.6	Delayed Drug Release	180
6.3.7	Biomaterial Surfaces	181
6.3.8	Biocides	181
6.3.9	Chromatographic Supports	182
6.4	Suppliers and Commercial Grades	183
6.5	Safety	183
	Tradenames	184
	References	185

7	Poly(vinylpyridine)	189
7.1	Monomers	189
7.2	Polymerization and Fabrication	191
7.2.1	Suspension Polymerization	191
7.2.2	Quaternization	191
7.2.3	Solution Polymerization	191
7.2.4	Spontaneous Polymerization	191
7.2.5	Dispersion Polymerization	193
7.2.6	Atom Transfer Radical Polymerization	193
7.2.7	RAFT Polymerization	195
7.2.8	Electropolymerization	195
7.2.9	Graft Polymerization	197
7.2.10	Poly(vinylpyridine <i>N</i> -oxide)	199
7.3	Properties	199
7.3.1	Miscibility	199
7.3.2	Thermal Properties	201
7.3.3	Pharmaceutical Properties	202
7.4	Applications	203
7.4.1	Adhesion Promoters	203
7.4.2	Dye Transfer Inhibitors	204
7.4.3	Catalysts	209
7.4.4	Toner Resins	212
7.4.5	Photolithography	212
7.4.6	Optoelectronic Devices	213
7.4.7	Chromatographic Resins	215
7.4.8	Ion Exchange Membranes	223
7.4.9	Sensor Techniques	226
7.4.10	Oilfield Applications	228
7.4.11	Lubricating Additives	229
7.4.12	Corrosion Inhibition	229
7.5	Suppliers and Commercial Grades	230
7.6	Safety	230
7.7	Environmental Impact and Recycling	232
7.7.1	Biodegradable Poly(styrene)	232
7.7.2	Bacterial Coagulants	232
	Tradenames	233
	References	238

8	Poly(vinylimidazole)	251
8.1	Monomers	251
8.1.1	Comonomers	252
8.2	Polymerization and Fabrication	253
8.2.1	Solution Polymerization	253
8.2.2	Precipitation Polymerization	254
8.2.3	Grafting	254
8.2.4	Organic-inorganic Hybrid Materials	255
8.3	Properties	255
8.4	Applications	255
8.4.1	Lithographic Printing	255
8.4.2	Printing Inks	257
8.4.3	Dye Transfer Inhibitors	257
8.4.4	Adhesive Compositions	259
8.4.5	Lubricating Additives	260
8.4.6	Additives for Electrolytes	261
8.4.7	Sensors	261
8.4.8	Enzyme Related Technology	262
8.4.9	Protein Purification	268
8.4.10	Hydrogels	270
8.4.11	Composite Membranes	271
8.4.12	Drug Uses	272
8.4.13	Cosmetic Compositions	275
8.5	Suppliers and Commercial Grades	277
8.6	Safety	278
	Tradenames	278
	References	282
9	Poly(vinylpyrrolidone)	293
9.1	Monomers	293
9.2	Polymerization and Fabrication	296
9.2.1	Homopolymerization	296
9.2.2	Copolymers	297
9.3	Properties	301
9.3.1	Fikentscher K Value	302
9.3.2	Miscible Blends	303
9.3.3	Optical Properties	304
9.4	Special Additives	304

9.4.1	Antioxidants	304
9.5	Applications	304
9.5.1	Medical Devices	306
9.5.2	Laundry Detergents	312
9.5.3	Adhesives	312
9.5.4	Membranes	314
9.5.5	Cleaning Compositions	317
9.5.6	Oil Field Applications	318
9.5.7	Photoresist Resin Compositions	320
9.6	Suppliers and Commercial Grades	323
9.7	Safety	324
9.8	Environmental Impact and Recycling	324
9.8.1	Biodegradable Polymers	324
	Tradenames	324
	References	331
10	Other Cationic Polymers	343
10.1	Manufacture	343
10.1.1	Bifunctional Quaternization	343
10.1.2	Addition Polymerization	345
10.1.3	Ring Opening Polymerization	347
10.1.4	Cationic Modification of Polymers	347
10.2	Applications	348
10.2.1	Superabsorbent Hydrogels	348
10.2.2	Paper Coatings for Ink Jet Printing	349
10.2.3	Water Purification	350
10.2.4	Cosmetic Compositions	352
10.2.5	Oil Field Applications	354
	Tradenames	354
	References	362
11	Other Anionic Polymers	367
11.1	2-Acrylamido-2-methyl-1-propane sulfonic acid	367
11.1.1	Copolymers	367
11.1.2	Oil Field Applications	368
11.1.3	Electroluminescent Devices	371
11.1.4	Chemoembolotherapy	372
11.2	Poly(sulfonic acid)s	372
11.2.1	Poly(vinylsulfonic acid)	372

11.2.2	Poly(4-vinylbenzoic acid)	374
11.2.3	Poly(styrene sulfonic acid)	376
11.3	Sulfonated Asphalt	377
11.3.1	Drilling Fluids	378
11.4	Lignosulfonate	378
11.4.1	Biopenetrants	378
	Tradenames	379
	References	381
Index		385
	Tradenames	385
	Acronyms	413
	Chemicals	419
	General Index	431

1

Poly(ethylene oxide)

Poly(ethylene oxide) (PEO) is sometimes addressed as poly(ethylene glycol) (PEG). This came about because it can be considered as being derived from the etherification of ethylene glycol (EG) into the polymer. On the other hand, the industrial synthesis, as explained below, starts with ethylene oxide (EO). We will use both names simultaneously, in the same way, as given in the references.

PEG was first studied by Lourenço in 1861 (1). He reported the synthesis of oligomeric PEGs up to hexaethylene glycol. It seems to be the first example of a condensation polymerization reaction at all (2). The first patents appeared around 1930 (3,4). Soon afterwards PEGs were used as components for poly(urethane)s (5).

1.1 Monomers

The basic monomers for PEO are shown in Table 1.1. The structures

Table 1.1 Monomers for Poly(ethylene oxide) Types

Monomer	Remarks
Ethylene oxide	Basic Monomer
Propylene oxide	Less water soluble
Butylene oxide	Less water soluble
Glycidol	Branched structures (6)
Ethoxy ethyl glycidyl ether	Branched structures (6)

are shown in Figure 1.1.

The basic monomer is EO. According to the nomenclature of heterocycles, EO is also addressed as oxiran. EO is synthesized by

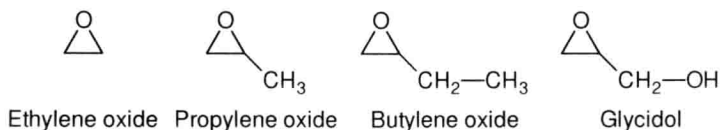


Figure 1.1 Monomers used for Poly(ethylene oxide)

the addition of oxygen to ethene. Propylene oxide or trimethylene oxide may also be used as comonomer together with EO. However, these comonomers should be used only in those small amounts as not to render the resulting copolymer water insoluble. Glycidol is a suitable comonomer for branched structures.

1.2 Polymerization and Fabrication

Water-soluble PEO is prepared by the ring opening polymerization of EO, usually in the presence of a small amount of an initiator such as low molecular weight glycol or triol alcoholate (7). Examples of such initiators include alcoholates of EG, diethylene glycol and other oligomers. Branched types are synthesized with multifunctional alcoholates, such as the potassium salts of glycerol, pentaerythritol, dipentaerythritol, or sorbitol (8). The basic mechanism is shown in Figure 1.2, top.

In Figure 1.2, bottom, the reaction of glycidol is shown. After addition, the negative charge may change its position, which causes the growth from both ends. In the course of the reaction a pendant hydroxyl group may again be activated as it turns into an alcoholate. This leads again to a growth reaction. In this way, branched structures are formed.

EO or various epoxides, and other cyclic ethers can be polymerized with anionic, cationic, and coordination catalysts. For the commercial production of polymer of such type, the most effective catalysts found are $(\text{CH}_3)_3\text{N}$ and SnCl_4 , CaCO_3 , FeCl_3 . Other compounds with catalytic activity are NaNH_2 , ZnO , SrO , and CaO (8).

The living polymerization techniques are preferred in comparison to other methods because molecular weight and polydispersity can be better controlled. The polymerization of EO can be carried