Volume 2

Handbook of Engineering and Specialty Thermoplastics

Water Soluble Polymers

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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

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Johannes Fink
20th January 2011

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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

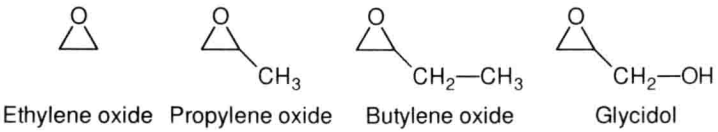

Figure 1.1 Monomers used for Poly(ethylene oxide)

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 strictures 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 $(CH_3)_3N$ 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