

Polyvinyl Alcohol

Properties and Applications

Edited by

C. A. FINCH

Polyvinyl Alcohol

Properties and Applications

Edited by

C. A. FINCH

Croda Polymers Ltd., Luton

A Wiley-Interscience Publication

JOHN WILEY & SONS

London · New York · Sydney · Toronto

Copyright © 1973 John Wiley & Sons Ltd. All Rights Reserved. No part of this publication may be reproduced, stored in a retrieval system, or transmitted, in any form or by any means, electronic, mechanical photo-copying, recording or otherwise, without the prior written permission of the Copyright owner.

Library of Congress catalog card number 72-8599

ISBN 0 471 25892 X

Printed in Great Britain by J. W. Arrowsmith Ltd., Bristol

Contributing Authors

- B. Duncalf** *Department of Printing Technology, Manchester Polytechnic, Manchester M15 6BR, England.*
- A. S. Dunn** *Department of Chemistry, University of Manchester Institute of Science and Technology, Manchester M60 1QD, England.*
- C. A. Finch** *Croda Polymers Ltd., Luton, Bedfordshire, England.*
- E. V. Gulbekian** *Vinyl Products Ltd., Carshalton, Surrey, England.*
- Howard C. Haas** *Research Laboratories, Polaroid Corporation, Cambridge, Mass. 02139, U.S.A.*
- Hiroshi Kishimoto** *Nippon Gohsei Co. Ltd., Osaka, Japan.*
- Yasuhumi Murakami** *Nippon Gohsei Co. Ltd., Osaka, Japan.*
- K. Noro** *Nippon Gohsei Co. Ltd., Osaka, Japan.*
- G. E. J. Reynolds** *Vinyl Products Ltd., Carshalton, Surrey, England.*
- K. Toyoshima** *Kuraray Co. Ltd., Osaka, Japan.*
- Kaname Tsunemitsu** *Nippon Gohsei Co. Ltd., Osaka, Japan.*
- Robert K. Tubbs** *Electrochemicals Department, Research Division, E. I. du Pont de Nemours and Company, Wilmington, Delaware, U.S.A.*
- Heinz Winkler** *Wacker-Chemie G.m.b.H., Burghausen, Germany.*
- Ting Kai Wu** *Electrochemicals Department, Research Division, E. I. du Pont de Nemours and Company, Wilmington, Delaware, U.S.A.*

Acknowledgements

This book is the result of a collaborative effort by many workers in different countries. Thanks are due to all the authors concerned, and also to many of their colleagues who have helped with specific aspects. The origin of the chapters by Dr. Toyoshima is mentioned in the Introduction; the translations on which these sections are based were arranged with the help of his colleagues, Dr. M. Shiraishi and Dr. S. Imoto, of the Kuraray Co. Ltd. (formerly the Kurashiki Rayon Co. Ltd.). Dr. K. Noro, of Nippon Gohsei Ltd., has been particularly helpful in proving preprints and information from Japanese sources. The U.K. agents of each of these companies were also most helpful in establishing the original contacts from which the book was planned.

I must take responsibility for any inaccuracies in the chapters by Japanese authors, because of the difficulties of distance and language, although proofs have been seen by the authors.

I am also grateful to several colleagues and former colleagues for their help, notably Dr. G. S. Park (for commenting on Chapter 14), Mr. D. H. Kidman (for help with Appendix 3) and Dr. A. Jobling (who has been a valuable sounding board for ideas developed during the preparation of the book). My wife has also helped in preparing a difficult typescript, which the publishers have accepted without flinching.

It is too much to hope that a book of this nature will be free from error; I would be most interested to have comments and suggestions of any way in which it could be improved.

C. A. FINCH

Foreword

PROFESSOR EM ICHIRO SAKURADA

Polyvinyl alcohol was first synthesized in Germany by Hermann and Haehnel in 1924, and a scientific paper was published in 1927, which contained not only methods of preparation, but also a description of the chemical and physical properties of the polymer. The use of polyvinyl alcohol as a stabilizer in the preparation of colloid systems was also suggested. Several years later, patents for the manufacture of threads, cords, tubes, etc., for medicinal purposes, and especially for sutures in surgery, were claimed.

During the 1930s, the Du Pont Company introduced polyvinyl alcohol commercially in the United States, the Wacker Company in Germany produced polyvinyl alcohol filament for sutures called 'Synthofil', and research workers in Japan published their first report on the manufacture of textile fibres from the polymer.

After the Second World War, the production of polyvinyl alcohol increased steadily, because of its importance in the production of synthetic textile fibre and its various uses as a cheap water-soluble polymer with unique properties. It is rather surprising that, in view of the rapid progress of research on polyvinyl alcohol, and its wide applications, only a few monographs on polyvinyl alcohol have been published.

It is, therefore, pleasing that Dr. Finch has edited a book on polyvinyl alcohol in collaboration with many excellent scientists working with polyvinyl alcohol. He has asked me to write a foreword to the book, perhaps because of my long involvement with polyvinyl alcohol, and I greatly appreciate his kind invitation. I also acknowledge the kindness of Mr. Okuda, of Kobunshi Kankokai, who has willingly allowed Dr. Toyoshima and his colleagues to base several sections of this book on their accounts in the recent Japanese language book on polyvinyl alcohol published by Kobunshi Kankokai.

I. SAKURADA

*Department of Polymer Science
Kyoto University
22 January 1972*

Introduction

C. A. FINCH

This book is the first attempt at a comprehensive treatment, in a Western language, of polyvinyl alcohol—a polymer of major and diverse industrial importance. World production of the polymer will be approaching 500,000 tonne per year by the time these words are published. Applications of the polymer are varied; many of them are discussed in the following pages.

Its fundamental properties are complex. Polyvinyl alcohol shows the behaviour expected of a vinyl polymer, with all the complications of stereoregularity and grafted structures, together with some of the properties of polyhydroxyl compounds which provide possible analogies with those of carbohydrates. In addition, the special properties of partly hydrolysed polyvinyl alcohols, which are, in effect, copolymers of vinyl acetate and the (hypothetical) vinyl alcohol monomer, must also be considered. It thus appeared desirable that a collaborative venture should be arranged, so that several authors could present a text that would provide both signposts and detail for readers working in academic and industrial environments.

The aim of the book is to inform specialist polymer scientists of the properties and individualities of a particularly interesting group of polymers, and to point out the considerable areas where the relations between structure and properties remain uncertain. At the same time, it is hoped that workers in industry will find useful information in the chapters devoted to specific applications, where relations between fundamental polymer-properties and particular end uses are described.

The first book on polyvinyl alcohol was written over thirty years ago¹ by a patent agent, and reflects the considerable interest in moulding applications and in its possible replacement of rubber—applications of the polymer which were proposed during an immediately after the Second World War. These applications are no longer significant. Other books more recently published include one in Russian,² several in Japanese,³⁻⁵ a reprint of a symposium held in Bradford in 1967,⁶ and, most recently, a short text⁷ on scientific aspects of fully hydrolysed polyvinyl alcohol. Apart from this

fairly sparse, and mostly rather inaccessible, literature, some useful review articles^{8,9} have appeared. Other review articles mentioned elsewhere in the book and several booklets from the manufacturers of polyvinyl alcohol represent the rest of the available information.

Two applications of polyvinyl alcohol have been deliberately omitted. These are the use of the polymer as a fibre (although the important application of sizing of yarns of other textiles is discussed), since its commercial development has largely been confined to Japan, and scientific aspects have been well described by Osugi,¹⁰ and the application of polyvinyl alcohol in medicine, which have been discussed elsewhere,^{7,11} giving the impression that this application, once promising, is now of little practical importance.

Throughout the book, contributing authors have been encouraged to provide extensive reference to the Japanese literature. Where possible, references to *Chemical Abstracts* have been provided, but coverage before about 1960 is notably incomplete, especially with patents, and, even after that date, it will be found that the very brief abstracts printed often contain less information than is provided in this book. Indeed, much of the detail provided in certain chapters by Japanese authors is appearing in a form accessible to the Western reader for the first time. The chapters by Toyoshima have been derived from a series of articles in *Kobunshi Kako*, which have subsequently been published as a book.⁵ I have extensively adapted a translated version to suit the purposes of the present book. In particular, Chapters 14 and 15 contain significant information previously available only in Japanese patents and literature.

The statistics of polyvinyl alcohol production are, by their nature, liable to change. However, an approximate idea of the growth in importance of the polymer can be gained from Tables I.1, I.2 and I.3. The most notable feature is the dominance of Japanese production. The original reasons for this were two fold.¹² The Japanese carbide industry was dominant during the important formative years, providing ample supplies of acetylene, and hence acetic acid and vinyl acetate. At the same time, technical and commercial development of polyvinyl alcohol fibres took place. Nearly half of the total production of polymer was used in this application. In recent years, applications other than fibres (which also appear to have been produced in Eastern Europe in small quantities⁹) have become relatively more important.

In accordance with suggestions previously made in the Bradford symposium monograph,⁶ the abbreviations PV-OH (polyvinyl alcohol) and PV-OAc (polyvinyl acetate) have been used where necessary. I believe this to be the simplest and most satisfactory way of distinguishing between the two polymers. The term 'PV-OH' is taken to include both fully and partly hydrolysed grades, although it is not, strictly speaking, accurate in the

latter case, and the term is qualified wherever possible. In accordance with this convention V-OH and V-OAc are used, where necessary, as abbreviations for the respective monomers.

Table I.1. Production capacity for polyvinyl alcohol (tonne per year)^a. World total capacity: approximately 460,000 tonne per year.

	1968	1970	1971	1972 (proposed)
Japan				
Kuraray Co		93,000	124,000	
Nippon Gohsei Co		33,600	65,000	
Denki Kagaku Co		23,000	29,000	
Unitika Chemical Co		24,000	24,000	
Shin-Etsu Chemical Co		9,000	9,000	
		182,600	251,000	
Western Europe				
France				
Rhône-Poulenc	6,000			30,000 ^a
West Germany				
Hoechst	3,750			28,000
Wacker	5,000			5,000
United Kingdom				
Revertex	2,700			2,700
Italy				
Montedison	3,000			3,000
Holland				
AKZO				24,000 ^a
Spain				
U.E.R.T.	1,500			1,500
	21,950			94,150
U.S.S.R. ^b		20,000		
China ^{c,*}	10,000	10,000		
U.S.A.				
Air Reduction ^d		15,000		15,000
Borden		4,000		4,000
Du Pont		14,000 ^e		65,000 ^e
Monsanto ^f		6,000		6,000
		39,000		90,000

^a Sources: *Chimie-Actualities*, 12 July 1971, pp. 11-14; *Oil, Paint and Drug Reporter (Chemical Marketing)*, 1 April 1970; Private communications.

^b At Yerevan, Armenia.

^c Partly used for fibre production.

^d Now Air Products and Chemical Inc.

^e Estimated.

^f Formerly Shawinigan Resins Inc.

^{*} A 30,000 t/yr plant is to be built in China by Unitika Chemical Co. (*Chemical Age*, 21 Sept. 1972).

^h Delayed.

Table I.2. Production of polyvinyl alcohol in Japan (tonne per year)^a

	Output	Capacity	Amount used for fibres
1950	594		
1951	3,341		
1952	3,108		
1953	4,645		
1954	4,686		
1955	7,015		
1956	11,813		
1957	16,965		
1958	16,314		
1959	21,573		
1960	28,116		
1961	42,161		
1962	55,546	81,000	35,400
1963	61,195		37,400
1964	69,399	85,000	36,000
1965	65,000		49,100
1966	92,500		54,100
1967	114,000		61,700
1968	142,100	135,000	72,000
1969	164,600	175,000	81,600
1970	188,890	205,000	94,579
1971	200,000	228,000	

^a Source: Nippon Sakubi Konwakai and private communications.

Table I.3: Production and consumption of polyvinyl alcohol (tonne per year)^a

	USA		West Germany		France		Italy		Holland		U.K.	
	Prod.	Cons.	Prod.	Cons.	Prod.	Cons.	Prod.	Cons.	Prod.	Cons.	Prod.	Cons.
1964			4800	3900	3000	3000	1400	2200	100	650		
1965	16,600	17,200										
1966	17,300	21,700	5800	4600	3500	3200	1800	2700	100	900		
1967	19,500	26,800										
1968	20,000	31,000	3500	6000	6000	6000	2800	4000			1000	2700
1969	25,000											5000
1970	22,000			7000		4600		4000		1500		
(estimated)												

^a Source: JETRO, 1969, and private communications.

REFERENCES

1. F. Kainer, *Polyvinylalkohole*, Ferdinand Enke Verlag, Stuttgart, 1949.
2. S. N. Ushakov, *Polyvinyl Alcohol and its Derivatives*, Vols. 1 and 2, Izdatel. Akad. Nauk SSSR, Leningrad, 1960.
3. I. Sakurada (Ed.), *Polyvinyl alcohol. First Osaka Symposium*, Kobunshi Gakkai, Tokyo, 1955.
4. *Polyvinyl alcohol. Second Osaka Symposium*. Kobunshi Gakkai. Tokyo, 1958 (a private translation of these texts has been prepared in the U.S.A.).
5. K. Toyoshima *et al.*, *Polyvinyl Alcohol*, Kobunshi Kankokai, Kyoto, 1970 (reprinted papers from *Kobunshi Kako*, Vols. 18 and 19).
6. C. A. Finch (Ed.), *Properties and Applications of Polyvinyl Alcohol*, Monograph No. 30, Society of Chemical Industry, London, 1968.
7. J. G. Pritchard, *Poly(vinyl alcohol). Basic properties and applications*, Gordon and Breach, London, 1970.
8. H. Warson, 'Poly(vinyl alcohol)', in S. A. Miller (Ed.), *Ethylene*, Ernest Benn Ltd., London, 1969, pp. 1019-1051.
9. M. K. Lindemann, 'Vinyl alcohol polymers', in *Encyclopedia of Polymer Science and Technology*, Vol. 14, Interscience, New York, 1971.
10. T. Osugi, 'PVA fibers', in *Man-Made Fibers, Science and Technology* (Eds. H. Mark, S. M. Atlas and E. Cernia), Vol. 3, Interscience, New York, 1968, pp. 245-302.
11. F. O. W. Meyer, *Pharmazie*, **4**, 264 (1949).
12. S. Murahashi, *Pure & Applied Chem.*, **15**, 435 (1967).

Contents

Introduction	
<i>C. A. Finch</i>	xiii
1. Historical Development of Polyvinyl Alcohol	
<i>Heinz Winkler</i>	1
2. General Properties of Polyvinyl Alcohol in Relation to its Applications	
<i>K. Toyoshima</i>	17
3. Manufacture of Polyvinyl Acetate for Polyvinyl Alcohol	
<i>K. Noro</i>	67
4. Hydrolysis of Polyvinyl Acetate to Polyvinyl Alcohol	
<i>K. Noro</i>	91
5. Manufacturing and Engineering Aspects of the Commercial Production of Polyvinyl Alcohol	
<i>K. Noro</i>	121
6. Preparation of Polyvinyl Alcohol from Monomers other than Vinyl Acetate	
<i>K. Noro</i>	137
7. Preparation of Modified Polyvinyl Alcohol from Copolymers	
<i>K. Noro</i>	147
8. Thermal Properties of Polyvinyl Alcohol	
<i>Robert K. Tubbs and Ting Kai Wu</i>	167
9. Chemical Properties of Polyvinyl Alcohol	
<i>C. A. Finch</i>	183
10. Stereochemistry of Polyvinyl Alcohol	
<i>C. A. Finch</i>	203
11. Use of Polyvinyl Alcohol in Warp Sizing and Processing of Textile Fibres	
<i>Kaname Tsunemitsu and Hiroshi Kishimoto</i>	233
<i>With added contribution by K. Toyoshima</i>	

12. Use of Polyvinyl Alcohol in Paper Manufacture <i>Kaname Tsunemitsu and Yasuhami Murakami</i> <i>With added contribution by K. Toyoshima</i>	277
13. Reactions of Polyvinyl Alcohol with Clay <i>K. Toyoshima</i>	331
14. Properties of Polyvinyl Alcohol Films <i>K. Toyoshima</i>	339
15. Acetalization of Polyvinyl Alcohol <i>K. Toyoshima</i>	391
16. Applications of Polyvinyl Alcohol in Adhesives <i>K. Toyoshima</i>	413
17. Polyvinyl Alcohol in Emulsion Polymerization <i>E. V. Gulbekian and G. E. J. Reynolds</i>	427
18. Photosensitized Reactions of Polyvinyl Alcohol used in Printing Technology and Other Applications <i>B. Duncalf and A. S. Dunn</i>	461
19. Polyvinyl Alcohol in Optical Films <i>Howard C. Haas</i>	493
20. Moulded Products from Polyvinyl Alcohol <i>K. Toyoshima</i>	523
21. Miscellaneous Applications of Polyvinyl Alcohol <i>K. Toyoshima</i>	529
Appendix 1. Compatibility of Polyvinyl Alcohol with Other Water-soluble High Polymers <i>K. Toyoshima</i>	535
Appendix 2. Preparation of Polyvinyl Alcohol Solutions <i>K. Toyoshima</i>	555
Appendix 3. Analytical methods for Polyvinyl Alcohol <i>C. A. Finch</i>	561
Name Index	573
Subject Index	598

CHAPTER 1

Historical Development of Polyvinyl Alcohol

HEINZ WINKLER

1.1. INTRODUCTION.....	1
1.2. PRODUCTION OF MONOMERS.....	1
1.3. PRODUCTION OF POLYMERS.....	2
1.4. STRUCTURE OF POLYVINYL ALCOHOL.....	10
1.5. CONCLUSION.....	13
1.6. REFERENCES.....	13

1.1. INTRODUCTION

Polyvinyl alcohol was the first totally synthetic colloid. It was first prepared from polyvinyl esters in 1924 by Herrmann and Haehnel.^{1,2} Today, the polymer is available in many different grades, varying in their degree of polymerization and of hydrolysis.

1.2. PRODUCTION OF MONOMERS

Carbide acetylene has been known for many years, and its conversion into acetaldehyde was first carried out in the last century—it is mentioned in the laboratory studies of Erdmann and Köttner (1898), and in two German patent applications by Wunderlich in 1907, which were not further pursued. The Consortium für Elektrochemische Industrie, under the direction of Mugdan, also carried out work in this field, and a survey published in 1932 stated:

‘The technical production of acetaldehyde from acetylene and water was investigated in 1910 both by the Consortium für Elektrochemische Industrie (Wacker-Chemie) and by Grünstein (Griesheim-Elektron) using mercury as the catalyst. Whilst Grünstein, using a discontinuous, and, therefore, an impractical, method, was unsuccessful, the Consortium showed, in a method which is still one of the most economic today, that continuous operation was possible, recycling acetylene in a circuit with acetaldehyde, with return of the acetylene unconsumed in the process.’³

This process, by Baum and Mugdan,^{4,5} was—apart from the preparation of acetaldehyde by the reduction of ethanol—first employed for the direct

oxidation of acetylene to acetaldehyde by Smidt, Hafner, Sedlmeier, Jira and Rüttinger in 1959.⁶⁻⁸ As the production of acetic acid by the oxidation of acetaldehyde had been established successfully by Mugdan and Galitzenstein in 1911,^{9,10} the production of vinyl acetate monomer (for use as a starting material for the manufacture of polyvinyl and polyvinyl alcohol, Figure 1.1) by various routes was possible. This development took some years. The First World War concentrated work on acetaldehyde and acetic acid exclusively—the latter was converted to acetone using a cerium salt as a catalyst. Immediately after the end of the war, work on the vinyl derivatives was restarted.

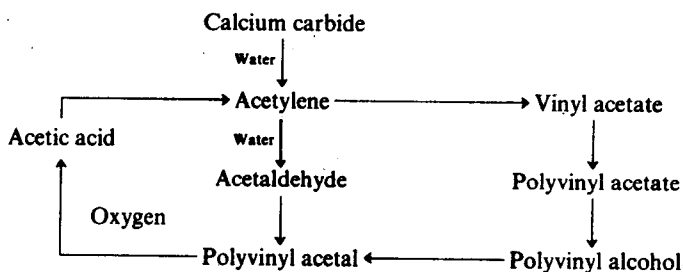


Figure 1.1

F. Klatte had already discovered and polymerized the vinyl esters at Greisheim-Elektron in 1910, mainly working with vinyl chloroacetate. The original applications of the 'Mowiliths' were as umbrella handles and knobs, which were already on the market, made with 'Galalith' and Bakelite. There was only slight interest in the paint and adhesives industries.¹¹ In addition, there was no technically satisfactory synthesis of the monomer. This was first developed in 1924, by Baum, Deutsch and Herrmann, using a mercury-containing catalyst. In 1927, the same workers improved the method, with a mercury-free system, which was known as the 'thermal-vinylation' method. The thermal vinylation of acetic acid was developed into an elegant method soon employed in Germany and other countries.

1.3. PRODUCTION OF POLYMERS

The starting material for the production of polyvinyl alcohol is not the monomer, but a polymerized ester. The polymerizations by which such esters are prepared are well known to be exothermic. In particular, the addition of large quantities of monomer leads, after a slow start, to a build up of heat which is sometimes explosive. However, the possible utility of catalytically initiated polymerizations was not at first understood, so that thermal polymerizations were carried out in light glass vessels, with reaction

times of up to a week. Using these conditions for the production of the polymer, the breakage rate of the glass vessels was high. All these difficulties are mentioned in the Greisheim-Elektron patents.¹²⁻¹⁴ Hoechst also began to investigate polymerization in 1923. Following experiments in autoclaves, the catalytic effects of peroxides and the regulating effect of acetaldehyde were discovered.¹⁵ In consequence, work could be carried out in open vessels, although practical difficulties limited the scale to 100 kg.¹⁷

The importance of the purity of the starting material was not fully realized, and attempts were made to produce high-molecular-weight polymers from impure monomers by methods which are now known to be impossible. In the years after the First World War, pure starting materials were expensive in comparison with established products of natural origin. Today, the high purity available in many pharmaceuticals is also in demand for many raw materials required for the production of relatively low-value end products.

The breakthrough took place in 1925, when Haehnel and Herrmann discovered methods for the safe polymerization of large quantities of vinyl acetate^{18,19} (Figure 1.2). Today, there are three principal methods for the

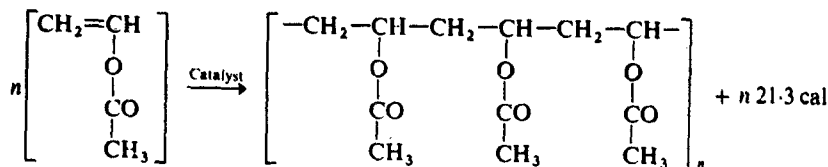


Figure 1.2

polymerization of vinyl acetate: bulk or mass polymerization, solution polymerization, and suspension or emulsion polymerization, all of which have been employed for the production of polyvinyl alcohol. Nowadays, the structures, synthesis, and reaction mechanisms of the compounds are well understood, thanks to the efforts of many different workers. However, in the 1920s, the position was different. The simple polymerization reaction was known, but the distinction between polyaddition and polycondensation was not realized until the pioneering work of H. Staudinger was published. Because of the First World War, scientific research, in general, was held back, and, during the period of inflation following the war, little effort was available for scientific work. Each novel product was considered chiefly in terms of its possible applications.

Klatte had no lasting success with his polymerization. Both the Consortium and Hoechst took some time to place pure vinyl acetate on the market. It was therefore not surprising that chemists studied both the