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Typeset, printed and bound by Rapra Technology Limited Cover printed by Livesey Limited, Shropshire, UK This book is dedicated to the memory of Dr Jack Buist, an exceptional personality in the field of polyurethane chemistry and technology. His vision on the advanced technologies in the polyurethane industry, his brilliant scientific activity leading to unanimous worldwide recognition, the exceptional career at ICI Polyurethanes, his work as founding editor of the international journal, *Cellular Polymers and Progress* has had great impact on the general worldwide development of polyurethane chemistry and polyurethane technology in the last five decades of the twentieth century. Dr Jack Buist will be forever, one of polyurethane's great men and has truly earned his place alongside Professor Otto Bayer, Professor Kurt C Frisch, Dr Adnan AR Sayigh, Dr Carlo Fiorentini and Dr Guenter Oertel in the Polyurethane's Hall of Fame.

Preface

The first polyurethane synthesised by Dr Otto Bayer, in 1937, at IG Farbenindustrie (Germany), by the reaction of a polyester diol with a diisocyanate, opened a new way in macromolecular chemistry: that is the synthesis of polymers by a new reaction, called polyaddition reaction.

Polyurethanes, having a relatively short history, of slightly more than 65 years, became one of the most dynamic groups of polymers, and their use covers practically all the fields of polymer applications - foams, elastomers, thermoplastics, thermorigids, adhesives, coatings, sealants, fibres and so on. Polyurethanes are used in nearly every aspect of daily life, changing the quality of human life. Furniture, bedding, seating for cars, shoe soles, thermoinsulation for refrigerators and buildings, wood substitutes, packaging, and coatings, are only a few common examples of polyurethane use in every day life.

Polyurethanes are obtained by the reaction of an oligomeric polyol (low molecular weight polymer with terminal hydroxyl groups) and a diisocyanate (or polyisocyanate). The structure of the oligomeric polyol used for polyurethane manufacture has a very profound effect on the properties of the resulting polymer.

The present monograph is dedicated to these very important raw materials used to build the polyurethane polymeric architecture: and covers chemistry and technology of oligomeric polyol fabrication, properties of these hydroxyl terminated oligomers and the effects of the oligomeric polyol structure on the resulting polyurethane properties.

So as not to be confused over the term 'polyol' some explanations are necessary. Generally, the term 'polyol' is used, in organic chemistry, for low molecular weight organic substances, very clearly identified as molecular entities, having more than two hydroxyl groups, such as: glycerol, propylene glycol, sorbitol and so on. The term 'polyol', is frequently used in relation to polyurethane fabrication, for all polyhydroxylic intermediates used. To be very clear, the present monograph is a study exclusively focused on oligomeric polyols, particularly low molecular weight polymers with terminal hydroxyl groups, covered by the general term of 'oligo-polyols'. These oligo-polyols are not unique molecular species,

being similar to all the polymers: a mixture between homologue species with various molecular weights (they have a molecular weight distribution). These oligo-polyols have an average molecular weight, by contrast with the low molecular weight of the polyols from organic chemistry which have a clear and unique molecular weight. In the text of this monograph, if the chemical nature of oligo-polyol is known, before the name 'polyol' is used the chemical name of the oligomeric chain, such as: polyether polyols, polyester polyols, polycarbonate polyols, acrylic polyols, Mannich polyols and so on. If the oligomeric polyols, are discussed generally, the term used will be 'oligo-polyol'.

Many excellent monographs have been dedicated to polyurethanes and, of course, the oligo-polyols were described there, but in a very general manner. The present monograph goes into the details of oligo-polyols synthesis in depth, and explains the chemical and physico-chemical subtleties of all oligo-polyol fabrications.

A large variety of chemical reactions for the synthesis of oligo-polyols to build the chemical architecture of oligo-polyols are used, such as: ring opening polymerisation of cyclic monomers by anionic, cationic or coordinative mechanisms, polycondensation reactions (polyesterification, transesterification, Mannich reactions, phenol-aldehydes condensations and so on), alkoxylation, radical polymerisation, transformation of double bonds in hydroxyl groups, such as: epoxydation-hydrolysis, hydroxylation, hydroformylation, ozonolysis-reduction and so on), oxidation and amidation reactions. These varieties of chemical reactions need serious knowledge of organic and macromolecular chemistry and the author tries to explain, in a very simple and accessible manner, the very complex phenomena involved in oligo-polyol fabrication.

The scientific literature dedicated to oligo-polyols is really impressive and the majority of information is based on the patent literature. The scientific literature, dedicated exclusively to oligo-polyols for polyurethanes is unexpectedly scarce. As an immediate consequence, the present monograph is based especially on the patent literature and on the personal experience of the author, who has worked for more than 30 years, on the synthesis of oligo-polyols for polyurethanes. As mentioned before, there are excellent books dedicated to polyurethanes and an excellent book dedicated to the chemistry and technology of isocyanates. The present monograph, dedicated to the second very important component of polyurethane fabrication, oligo-polyols, tries to complete this series of monographs in a logical manner.

This book attempts to link in a general concept, organised in a systematic manner, the most important knowledge, data and information concerning the chemistry and technology of oligo-polyols for polyurethanes. This general point of view resulting from the fact that all oligo-polyols used for polyurethanes have many things in common, will be presented, in detail, in this monograph. In order not to provide too much information, and to avoid presentation of confidential data, the commercial names of the oligo-polyols are

not mentioned. Thus, each oligo-polyol is identified by the chemical structure or by the chemical name. At the same time and for the same reasons, the names of companies which developed and produced the various types of common oligo-polyols are not mentioned. The commercial name and the company name is specified exceptionally, only for the unanimously accepted very important developments in the area of oligo-polyols (e.g., PHD-polyols of BAYER and so on).

Of course, it is totally impossible to cover all the aspects and to describe all the oligopolyol structures created as a consequence of the impressive worldwide creative effort of research laboratories from companies, universities, research centers and institutes, but I am sure that the most important aspects of oligo-polyol manufacture are presented.

The present monograph is addressed to all specialists working in the area of oligo-polyols for polyurethanes: students, researchers, scientists, engineers, professors, experts from: industry, universities, research centers and research institutes.

I hope that the monograph will be the start for new and original and developments in the area of oligo-polyols for polyurethanes, including creation of totally new oligo-polyols, with a new design and new chemical architecture, and of course for new technologies and unconventional manufacturing technologies.

Good luck!

I express my profound gratitude to my wife Adriana for her continuous and unconditional help and support.

I am grateful to, and I thank very much Ms Frances Powers, Senior Commissioning Editor, Rapra Technology, for her tenacity, patience, attention, high competency and professionalism to review and correct each page, each table, each formula, each sentence, each reference, each word, each sign and to produce the book to such standard. I am also grateful to Frances, for the fact that all the time she believed in me, and in my capability to finish the book.

I would also like thank very much to the following members of Rapra's Publishing Department: Ms Claire Griffiths and Mrs Hilary Moorcroft (editorial assistants) and Mrs Sandra Hall for typesetting the book and designing the cover, all of whom have done a remarkable job, in producing such a high quality book.

Mihail Inonescu August 2005

Contents

1	Polyols				
	1.1	Introduction			
	References				
2	Basic	asic Chemistry of Polyurethanes			
	2.1	Reaction of Isocyanates with Alcohols			
	2.2	Reaction of Isocyanates with Water			
	2.3	Reaction of Isocyanates with Urethanes			
	2.4	Reaction of Isocyanates with Urea Groups			
	2.5	Reaction of Isocyanates with Carboxylic Acids			
	2.6	Dimerisation of Isocyanates			
	2.7	Trimerisation of Isocyanates			
	2.8	Reaction of Isocyanates with Epoxide Compounds			
	2.9	Reaction of Isocyanates with Cyclic Anhydrides			
	2.10	Prepolymer Technique			
	2.11	Quasiprepolymer Technique 24			
	2.12	One Shot Technique			
	2.13	Several Considerations on the Polyaddition Reaction			
	Refer	rences			
3 The General Ch		General Characteristics of Oligo-Polyols			
	3.1	Hydroxyl Number			
		3.1.1 Hydroxyl Percentage			
	3.2	Functionality			

	3.3	Molecu	ular Weight and Molecular Weight Distribution	39
	3.4	Equiva	llent Weight	40
	3.5	Water	Content	41
	3.6	Primar	y Hydroxyl Content	41
	3.7	Reactiv	vity	45
	3.8	Specific	c Gravity	47
	3.9	Viscosi	ity	47
	3.10	Colour	r	48
	3.11	Acid N	Number	48
	Refer	ences .		50
4	Oligo	-Polyol	s for Elastic Polyurethanes	55
	4.1.	Polyall	kylene Oxide Polyether Polyols	55
		4.1.1	Synthesis of Polyether Triols Based on Glycerol Homopolymers of PO	64
		4.1.2	Kinetics of PO Addition to Glycerol	
		4.1.3	Random Copolyethers PO-EO (Heteropolyether Polyols)	93
		4.1.4	Polyether Polyols Block Copolymers PO-EO	101
		4.1.5	Technology for Polyether Polyol Fabrication	119
	4.2 Anionic Polymerisation of Alkylene Oxides Catalysed by Phosphazenium Compounds			148
4.3 High Molecular Weight Polyether Polyols Based on Polyamine Starters. Autocatalytic Polyether Polyols			Molecular Weight Polyether Polyols Based on nine Starters. Autocatalytic Polyether Polyols	152
	Refer	erences		
5 Synthesis of High Molecular Weight Polyether Polyols with Double Metal Cyanide Catalysts (DMC Catalysts)			High Molecular Weight Polyether Polyols with Double de Catalysts (DMC Catalysts)	167
	References			
6	Polyr	ner Poly	yols (Filled Polyols)	185

	6.1	Graft I	Polyether Polyols	186
	6.2	The Cl	hemistry of the Graft Polyether Polyols Synthesis	187
		6.2.1	Generation in situ of NAD by Grafting Reactions	193
		6.2.2	Stabilisation of Polymer Dispersions in Polymer Polyols with Macromers (Reactive NAD)	197
		6.2.3	Nonreactive Nonaqueous Dispersants	204
		6.2.4	The Mechanism of Polymer Particle Formation in Polymer Polyols Synthesis by Radical Polymerisation	207
	6.3		echnology of Polymer Polyols Manufacture by al Processes	209
		6.3.1	Synthesis of Polymer Polyols by Using Preformed Aqueous Polymeric Lattices	214
	6.4	PHD F	Polymer Polyols (Polyurea Dispersions)	215
	6.5	Polyiso	ocyanate Polyaddition (PIPA) Polymer Polyols	219
	6.6	Other Polymer Polyols		
		6.6.1	Epoxy Dispersions	223
		6.6.2	Polyamide Dispersions	225
		6.6.3	Aminoplast Dispersions	226
	Refer	ences		227
7	Polye	ther Po	lyols by Cationic Polymerisation Processes	235
	7.1	Polyter	trahydrofuran (Polytetramethylene Glycols)	235
	7.2	High Molecular Weight Polyalkylene Oxide Polyols by Cationic Polymerisation		245
	7.3	Polyet	her Diols and Triols, Copolymers THF-alkylene Oxides	249
	Refer	ences		257
8	Polye	ster Po	lyols for Elastic Polyurethanes	263
	8.1	Chemi	stry of Polyester Polyol Synthesis	264
	8.2	Consid	deration of the Kinetics of Polyesterification Reactions	270

		8.2.1	Self Catalysed Polyesterification Reactions (Without Catalyst)	2.70
		8.2.2	Side Reactions in Polyesterification	
		8.2.3	Hydrolysis Resistant Polyester Polyols	
	8.3	Techno	ology for Polyester Polyols Fabrication	
			-caprolactone) Polyols	
	8.5		rbonate Polyols	
		•		
9	Polyl	outadien	ne Polyols	295
	9.1	Polybu	stadiene Polyols by Radical Polymerisation of Butadiene	295
	9.2		sis of Polybutadiene Polyols by Radical erisation of Butadiene	299
	9.3		sis of Polybutadiene Polyols by Anionic erisation of Butadiene	301
	Refer	ences .		303
10	Acry	lic Polvo	ols	305
	References			
11	Polys	iloxane	Polyols	311
	Refe	rences		315
12	Polyc	ols for R	Rigid Polyurethanes - General Considerations	317
	Refe	rences		319
13	Polve	ether Po	lyols for Rigid Polyurethane Foams	321
	-		olyaddition of Alkylene Oxides to Hydroxyl Groups	
	13.1		The Mechanism of Alkylene Oxide Polyaddition to	525
		13.1.1	Hydroxyl Groups Catalysed by the Tertiary Amines	326
	13.2	Polvetl	her Polyols Technologies for Rigid Foam Fabrication	336

		13.2.1	Anionic Polymerisation of PO (or/and EO) Initiated by Polyols which are Liquid at the Reaction Temperature	343
	13.3		Considerations Concerning the Alkoxylation of to Rigid Polyether Polyols	347
		13.3.1	Anionic Polymerisation of PO (or/and EO) Initiated by High Melting Point Polyols which are Solid at the Reaction Temperature	353
	Refer	ences		
14	Amir	nic Polyo	ols	371
	Refer	ences		379
1.5	D: :1	15.1.1		
15 Rigid Polyols Based on the Alkoxylation of Aromatic Compounds Condensates with Aldehydes				381
	15.1	Mannio	ch Polyols	381
	15.2	Novola	ık-Based Polyether Polyols	400
	15.3	Bispher	nol A Based Polyols	403
	15.4	Resorci	inol Based Diols	406
	15.4	Melam	ine-Based Polyols for Rigid Polyurethanes	407
	Refer	rences		414
16	Polye	ester Pol	yols for Rigid Polyurethane Foams	419
	16.1		tic Polyester Polyols from Bottom Residues ng in DMT Fabrication	421
	16.2		tic Polyester Polyols from Polyethylene thalate Wastes (Bottles, Films, Fibres)	422
	16.3	Aroma	tic Polyester Polyols Based on Phthalic Anhydride (PA)	424
	16.4		Methods for the Synthesis of Polyester Polyols for Goams	426
	Refer	rences		431

17 Polyols from Renewable Resources - Oleochemical Polyols			
	17.1 Vegetable Oil Polyols (Oleochemical Polyols)	443	
	17.1.1 Synthesis of Vegetable Oil Polyols by using Reactions Involving Ester Groups	450	
	17.1.2 Synthesis of Vegetable Oil Polyols by using Reactions Involving the Double Bonds	455	
	17.1.3 Other Reactions Involving Reactions of Double Bonds of Vegetable Oils	463	
	17.1.4 Other Renewable Materials	469	
	References	470	
18	Flame Retardant Polyols	477	
	18.1 Chlorine and Bromine Containing Polyols	481	
	18.2 Phosphorus Polyols	485	
	18.2.1 Esters of Ortho-Phosphoric Acid	485	
	18.2.2 Esters of Phosphorus Acid	486	
	18.2.3 Phosphonate Polyols	487	
	18.2.4 Phosphine Oxide Polyols	493	
	18.2.5 Phosphoramidic Polyols	494	
	References	496	
19	New Polyol Structures for Rigid Polyurethane Foams	501	
	19.1 Amidic Polyols	501	
	19.2 Hyperbranched Polyols and Dendritic Polyols	505	
	References	513	
20	Oligo-Polyols by Chemical Recovery of PU Wastes	515	
	20.1 Hydrolysis of PU Polymers	516	
	20.2 Glycolysis of PU Polymers	517	
	20.3 Aminolysis of PU Polymer	518	

	20.4	Alkoxylation of PU Polymer5	20	
	20.5	Chemical Recovery of Flexible PU Foam Wastes by Hydrolysis 5	22	
	20.6	Rigid Polyols by Glycolysis of Rigid PU Foam Wastes5	23	
	20.7	Rigid Polyols by Aminolysis of Rigid PU Foam Wastes5	25	
	20.8	Technology for Chemical Recovery of Rigid PU Foams (and Isocyanuric Foams) by the Glycolysis Processes	28	
	Refer	ences	31	
21	1 Relationships Between the Oligo-Polyol Structure and Polyurethane Properties			
	21.1	Molecular Weight5	35	
		21.1.1 The Effect of the Molecular Weight of Oligo-Polyols 5		
	21.2	Intermolecular Forces	38	
		21.2.1 The Effect of the Chemical Nature of Oligo-Polyol Chains 5	38	
	21.3	Stiffness of the Chain5	40	
	21.4	Crystallinity5	42	
	21.5	Crosslinking5	42	
		21.5.1 The Effect of Oligo-Polyol Functionality	42	
		21.5.2 The Effect of Oligo-Polyol Structure on the Polyurethane Behaviour in Contact with Organic Solvents and Water	54 <i>6</i>	
	21.6	Thermal Stability and Flame Retardancy5	47	
		21.6.1 Flame Retardancy5	48	
Pos	tface .	5	51	
Abl	orevia	ons 5	53	
Ind	ANZ.	5		