Future Trends in MODERN PLASTICS

ohannes Karl Fink

Scrivener Publishing



Future Trends in Modern Plastics

Scrivener Publishing

100 Cummings Center, Suite 541J Beverly, MA 01915-6106

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

Future Trends in Modern Plastics

Johannes Karl Fink Montanuniversität Leoben, Austria





This edition first published 2024 by John Wiley & Sons, Inc., 111 River Street, Hoboken, NJ 07030, USA and Scrivener Publishing LLC, 100 Cummings Center, Suite 541J, Beverly, MA 01915, USA © 2024 Scrivener Publishing LLC

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

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, photocopying, recording, or otherwise, except as permitted by law. Advice on how to obtain permission to reuse material from this title is available at http://www.wiley.com/go/permissions.

Wiley Global Headquarters

111 River Street, Hoboken, NJ 07030, USA

For details of our global editorial offices, customer services, and more information about Wiley products visit us at www.wiley.com.

Limit of Liability/Disclaimer of Warranty

While the publisher and authors have used their best efforts in preparing this work, they make no representations or warranties with respect to the accuracy or completeness of the contents of this work and specifically disclaim all warranties, including without limitation any implied warranties of merchantability or fitness for a particular purpose. No warranty may be created or extended by sales representatives, written sales materials, or promotional statements for this work. The fact that an organization, website, or product is referred to in this work as a citation and/or potential source of further information does not mean that the publisher and authors endorse the information or services the organization, website, or product may provide or recommendations it may make. This work is sold with the understanding that the publisher is not engaged in rendering professional services. The advice and strategies contained herein may not be suitable for your situation. You should consult with a specialist where appropriate. Neither the publisher nor authors shall be liable for any loss of profit or any other commercial damages, including but not limited to special, incidental, consequential, or other damages. Further, readers should be aware that websites listed in this work may have changed or disappeared between when this work was written and when it is read.

Library of Congress Cataloging-in-Publication Data

ISBN 9781394237548

Cover image: Pixabay.com Cover design by Russell Richardson

Set in size of 11pt and Minion Pro by Manila Typesetting Company, Makati, Philippines

Printed in the USA

10 9 8 7 6 5 4 3 2 1

Preface			xi
1	Moi	nomers and Polymerization Methods	1
	1.1	Types of Monomers and Synthesis Methods	2
		1.1.1 Alkylene Monomers	2
		1.1.2 Epoxide Monomers	5
		1.1.3 Diol-Based Monomers	8
		1.1.4 Diacid-Based Monomers	9
		1.1.5 Bio-Based monomers	9
		1.1.6 Fatty Acids	11
		1.1.7 Cyclic Fatty Acids	14
		1.1.8 Triglycerides	14
		1.1.9 Ester-Based Monomers	15
		1.1.10 Amino Acids	20
		1.1.11 Monosaccharides	20
		1.1.12 Nucleotides	27
	1.2	Polymerization Methods	28
		1.2.1 Anionic Polymerization	28
		1.2.2 Cationic Polymerization	28
		1.2.3 Plasma Polymerization	28
		1.2.4 Ring-Opening Polymerization	29
	1.3	Future Trends in Summary	29
		References	30
2	Aut	omotive Industry, Hemp and Sustainable Polymers	33
	2.1	Plastics Industry	33
	2.2	Fields of Application	35
	2.3	Evolution	35
	2.4	Material Safety	36
	2.5	Environmental Sustainability of Plastics	36
	2.6	Future Directions for Sustainable Polymers	37
		2.6.1 Hemp	37

vi Contents

	2.7	Circular Economy	40
		2.7.1 Food Waste	41
		2.7.2 Conversion of Waste Plastic into a Feedstock	44
	2.8	Automotive Industry	47
		2.8.1 Airbag	52
		2.8.2 Biomass Pellets	56
		2.8.3 Plastic Panels	59
		2.8.4 Automotive Interiors	62
		2.8.5 Automotive Glass Run	64
		2.8.6 Milling Burr Control Tape	65
	2.9	Future Trends in Summary	65
		References	65
3	Plas	tic Waste	73
	3.1	Valorization of Plastic Waste	73
	3.2	Origin of Plastic Waste	74
		3.2.1 Microplastics	74
		3.2.2 Plastic Waste from Food	75
		3.2.3 Toxic Products in Plastic Waste	77
		3.2.4 Medical Plastic Waste	80
	3.3	Waste Accumulation	81
		3.3.1 Reduction of Microplastic Waste Accumulation	81
	3.4	Conversion of Plastic Waste into Fuel	84
		3.4.1 Apparatus for the Conversion of Plastic Waste into Fuel	84
		3.4.2 Pyrolysis of Poly(ethylene)	87
		3.4.3 Pyrolysis for the Recovery of Aromatic Compounds	88
		3.4.4 Dechlorination of Mixed Plastics Pyrolysis Oils	90
		3.4.5 Hydrogen-Rich Fuel Gas	95
		3.4.6 Mixed Plastic Waste	95
	3.5	Future Trends in Summary	96
		References	96
4	Plas	tic Pollution in the Environment	101
	4.1	Ingestion of Macroplastics by Odontocetes of the Greek Seas	s 101
	4.2	Greenhouse Gas Emissions Associated with Plastics	
		Consumption	103
	4.3	Sustainability of Plastic Types	103
	4.4	Plastic Industry in China	105
	4.5	Carbon Footprint	108
	4.6	Global Greenhouse Gas Emission from Both	
		Traditional Plastics and Bioplastics	109

	4.7	Future Trends in Summary	110
		References	111
5	Rec	ycling	113
	5.1	The Frontier of Plastics Recycling	113
		5.1.1 Waste as a Resource for High-Value Applications	113
	5.2	Recycling Technologies	113
		5.2.1 Maintaining the Polymer Structure	114
		5.2.2 Chemical Safety Aspects	116
		5.2.3 Migration of Contaminants	117
		5.2.4 Migration of Plasticizers	119
		5.2.5 Migration of Aluminum and Silicon	120
		5.2.6 Delamination	120
		5.2.7 Separation	121
		5.2.8 Mechanical Recycling	121
		5.2.9 Selective Dissolution	122
		5.2.10 Dissolution/Reprecipitation Technique	123
		5.2.11 Compatibilization	124
		5.2.12 Feedstock Recycling	124
		5.2.13 Closed-Loop Recycling	125
		5.2.14 Supercritical Ethanol	127
	5.3	Plastic Waste Generation	128
	5.4	Recycled Plastics in Food Contact	128
		5.4.1 Improving Safety and Quality	128
	5.5	Enzyme Discovery and Engineering for Sustainable Plastic	
		Recycling	129
	5.6	Special Compositions	129
	5.7	Bottle Recycling	131
		5.7.1 PET Bottles	131
		5.7.2 Compatibilization of PET and PLA	133
	5.8	Recycling of Post-Consumer Polyolefins	134
		5.8.1 Predictive Models	134
		5.8.2 Safety Concerns	134
	5.9	Recycling of Multi-Material Multilayer Plastic Packaging	135
		5.9.1 Fast-Moving Consumer Goods	135
		5.9.2 Recyclability Enhancement of Food Containers	139
	5.10	Future Trends in Summary	139
	Refe	erences	140
6	Ren	ewable Energy	147
	6.1	Plastic Waste	147
		6.1.1 Strategy to Sort and Recycle Plastic Waste	147

	6.2	 6.1.2 Gasification System for Hydrogen Production 6.1.3 Renewable Energy and Plastic Waste Recycling 6.1.4 Greenhouse Gas Emission Future Trends in Summary References 	149 153 153 154 154
7	Met	hods of Characterization	157
	7.1	Polymer Identification Techniques	157
	7.2	Identification of the Materials	158
		7.2.1 Spectroscopic Methods	158
		7.2.2 Real-Time Mass Spectrometry	158
		7.2.3 Optical Identification	159
	7.3	Future Trends in Summary	160
		References	160
8	Med	ical Uses	163
	8.1	Optical Applications	163
	8.2	Materials	165
		8.2.1 Hydrogel Contact Lenses	166
	8.3	Surgery	170
		8.3.1 ChatGPT	171
		8.3.2 3D Bioprinting	173
	8.4	Polymer Implants	173
		8.4.1 Dexamethasone	173
	8.5	Orthopedic Applications	176
		8.5.1 Implant Metals	176
		8.5.2 Bioabsorbable and Degradable Polymeric Implants	176
		8.5.3 Bone	178
	8.6	Sutures	
	8.7	Biomedical Uses	178
		8.7.1 Coatings from Polysaccharides	178
	8.8	Drug Delivery	180
		8.8.1 Poly(lactic acid)	180
		8.8.2 Carrageenan	180
	8.9	Self-Healing Materials	180
	8.10	Surgical Instruments	181
		8.10.1 Tribological Properties of Polymers	101
	0.11	in Medical Devices	181
	8.11	Micropiastics	182
	8.12	Future Trends in Summary	183
		Keterences	183

9	Rest	oration	191
	9.1	Deterioration of Cultural Heritage	191
		9.1.1 Polymers Usage	191
	9.2	Science	192
		9.2.1 Polyelectrolytes	192
		9.2.2 Microbial Attack	194
		9.2.3 Synthetic Polymers	195
		9.2.4 Removal of Polymers	195
	9.3	Layer-by-Layer Architectures	197
		9.3.1 Polymers for Multilayer Architecture	197
	9.4	Future Trends in Summary	198
		References	198
10	Foo	d Applications	201
	10.1	Molecularly Imprinted Polymers	201
		10.1.1 Extraction of Tetracycline Residues	202
		10.1.2 Mycotoxins	203
	10.2	Self-Assembled Carbohydrate Polymers	206
	10.3	Quartz Crystal Microbalance Sensors	206
		10.3.1 Fabrication Methods	206
		10.3.2 Vapor Deposition	211
		10.3.3 Analyte-Responsive Polymers	214
		10.3.4 Specific Materials and Methods of Synthesis	217
		10.3.5 Detection of an Analyte in a Liquid Sample	218
		10.3.6 Detection of Gases and Humidity	219
	10.4	Analysis of Problematic Additives	221
		10.4.1 Pesticide Detection	221
		10.4.2 Aflatoxin in Milk	222
	10.5	Food Packaging	223
		10.5.1 Packaging Methods	223
		10.5.2 Heat-Sealable Food Packing Films	227
		10.5.3 Polymers for Food Packaging	231
		10.5.4 Polymer Membranes for Food Packaging	234
		10.5.5 Natural Colorants	237
	10.6	Food Container	238
	10.7	Future Trends in Summary	238
		References	239
11	Add	itive Classes	247
	11.1	Compatibilizers	247
	11.2	Contaminants	248
		11.2.1 Weathering of Plastic Materials	249

		11.2.2	Contaminants in Wastewater	249
		11.2.3	Removal of Pharmaceuticals Using Cyclodextrin	251
	11.3	Legacy	Additives	253
	11.4	Chain I	Extenders	253
		11.4.1	Multiblock Polymer	255
		11.4.2	Chain Extenders for Polyurea Polymer	255
	11.5	Nuclea	ting Additives	256
	11.6	Food A	dditives	258
		11.6.1	Mycotoxins	259
		11.6.2	Stabilizers	260
		11.6.3	Microbial Stabilizers	260
		11.6.4	Thickeners	261
		11.6.5	Gelling Agents	261
	11.7	Antiox	idants	263
		11.7.1	Natural Antioxidants	264
		11.7.2	Polyphenolic Antioxidants	265
		11.7.3	Mango Peel	266
	11.8	Future	Trends in Summary	266
		Referer	nces	267
12	Manu	ıfacturii	ng	271
	12.1	Wood-	Plastic Composites	271
		12.1.1	Fabrication	271
		12.1.2	Manufacturing Processes	272
		12.1.3	Properties	275
		12.1.4	Polymeric Materials	276
		12.1.5	Recycling	277
	12.2	Single-	Use Plastics	278
		12.2.1	Green Composites	278
		12.2.2	Diagnostic Waste	279
	12.3	Future	Trends in Summary	280
		Referer	nces	280
In	dex			283
	Acror	nyms		283
	$\mathbf{C}^{\mathbf{I}}$: 1		286
	Chem	licals		200

Preface

This book focuses on the issues concerning future trends in plastics.

The book begins with a chapter about monomers and polymerization methods. Here, newly developed monomers, such as alkylene-based monomers, epoxide monomers, diol-based monomers, bio-based monomers, and several other types, are discussed. Then, modern polymerization methods are explained, such as ionic polymerization, plasma polymerization, and ring-opening polymerization.

Then, in the next chapter, special issues and some future trends in the plastics industry are explained. Here, recommendations for future research, are also noted. Also discussed are the enormous benefits plastics have brought to society owing to their versatility, light weight, durability and low costs. However, these properties have come with negative externalities, especially because these persistent materials are leaked into the environment during their entire life cycle. Therefore, an important section is included on the future directions for sustainable polymers.

The valorization of plastic waste is an important feature of Chapter 4. Nowadays, polymers are the most versatile materials. They contain certain chemicals and additives, such as pigments, concentrates, anti-blockers, light transformers, UV-stabilizers, etc. Therefore, an in-depth analysis has been presented with respect to the recovery, treatment and recycling routes of plastic waste in Chapters 5 and 6.

The methods of characterization are detailed in Chapter 7. Here, the properties and material testing methods, such as standards, are described.

In Chapter 8, usage of plastics in medical devices are detailed. Here, the properties, requirements, and applications are presented along with a comprehensive overview of the main types of plastics used in medical device applications.

The subsequent Chapters and their subject matter are the use of plastics in restoration, food applications, additive classes and manufacturing. The text focuses on the literature of the past decade. Beyond education, this book will serve the needs of specialists who have only a passing knowledge of the subject matter but need to know more.

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 aspects, and it is recommended that the reader study the original literature for more complete information.

The reader should be aware that mostly US patents have been cited where available, but not the corresponding equivalent patents in other countries. For this reason, the author cannot assume responsibility for the completeness, validity or consequences of the use of the material presented herein. Every attempt has been made to identify trademarks; however, there were some that the author was unable to locate.

Index

There are three indices: 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, Friedrich Scheer, Christian Slamenik, and Elisabeth Groß for their support in literature acquisition. Also, many thanks to Boryana Rashkova for her nice support.

I also want to express my gratitude to all the scientists who have carefully published their results concerning the topics dealt with herein. 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. In addition, my thanks go to Jean Markovic, who made the final copyedit with utmost care.

> **Johannes Fink** Wiener Neustadt December 20, 2023

1

Monomers and Polymerization Methods

Several monomers are used for polymers. Most of them are old but some of them are fresh materials. Here, monomer types and monomers are given and also special methods for polymerization.

A lot of these materials are collected in books (1-6).

Monomers can be subdivided into two classes, depending on the kind of polymer that they form (7). Monomers that participate in condensation polymerization have a different stoichiometry than monomers that participate in addition polymerization. Classifications may also include (8):

- 1. Alkylene monomers
- 2. Epoxide monomers
- 3. Diols
- 4. Diacids
- 5. Amino acids
- 6. Alcohol acids
- 7. Bio-based monomers
- 8. Nucleotides
- 9. Monosaccharides
- 10. Natural monomers
- 11. Synthetic monomers
- 12. Polar monomers
- 13. Nonpolar monomers

1.1 Types of Monomers and Synthesis Methods

In this section, common monomers, both conventional and modern monomers, are shown.

1.1.1 Alkylene Monomers

Various monomer types are presented in Tables 1.1, 1.2, and 1.7 below. Also, these compounds are shown in Figures 1.1 and 1.2.

Compound	Compound
Ethylene	Propylene
1-Butene	1-Pentene
2-Butene	2,3-Dimethyl-1-butene
1-Pentene	2-Pentene
2-Methyl-1-butene	3-Methyl-1-butene
2-Methyl-2-butene	1-Hexene
2-Hexene	3-Hexene
2-Methyl-1-pentene	3-Methyl-1-pentene
4-methyl-1-pentene	2-Methyl-2-pentene
3-Methyl-2-pentene	4-Methyl-2-pentene
2,3-Dimethyl-1-butene	3,3-Dimethyl-1-butene
2,3-Dimethyl-2-butene	2-Ethyl-1-butene
<i>a</i> -Pinene	6,6-Dimethylbicyclo[3.1.1]hept-2-ene

Table 1.1 Monomers with one double bond.

 Table 1.2 Monomers with multiple double bonds.

Compound	Compound	Compound
Butadiene	Isoprene	Chloroprene
Norbornadiene	1,5-Cyclooctadiene	Dicyclopentadiene

Some modern alkene-based monomers are shown in Table 1.3.

1.1.1.1 Apopinene

Apopinene (6,6-Dimethylbicyclo[3.1.1]hept-2-ene), c.f. Figure 1.4, is a biorenewable monomer that can be used for ring-opening metathesis polymerization (9).

Monomers and Polymerization Methods 3





Figure 1.1 Monomers with one double bond.

Compound	Reference
Apopinene	(9)
6,6-Dimethylbicyclo[3.1.1]hept-2-e	ene (9)
Bio-based acrylic monomers	(10)

Table 1.3 Modern Monomers.

4 FUTURE TRENDS IN MODERN PLASTICS



Figure 1.2 Monomers with multiple double bonds.



Norbornadiene Dicy

Dicyclopentadiene

Figure 1.3 Cyclic monomers with multiple double bonds.



Figure 1.4 Apopinene.

Apopinene is the most abundant monoterpene present in nature and plays a crucial role in many biological, atmospheric and industrial processes. Similar to many other readily accessed and biorenewable terpenes, α -pinene is widely used in both the fine chemical and polymer industries. The Lewis acid-catalyzed polymerization of α -pinene generates a polymer and has found a variety of uses in a plethora of industrial applications such as adhesives, plastics, and rubbers.

The high abundance, low cost, and biorenewability of α -pinene make its incorporation into additional novel materials highly desirable from the standpoint of sustainability.

One avenue that has sparked some theoretical interest is the ring-opening metathesis polymerization of α -pinene (11).

1.1.2 Epoxide Monomers

Various epoxide monomers are presented in Table 1.4. Some of these monomers are also shown in Figure 1.5.

The synthesis of functionalized polycarbonates, employing mainly propylene oxide and cyclohexene oxide, has been detailed (12). In recent years, functionalized polycarbonates have become an emerging topic with a broad scope of potential applications. The synthetic routes and properties of numerous functionalized polycarbonates synthesized from CO_2 and functional epoxide monomers have been described (12).

The synthesis of polymers from renewable resources is of high interest. Polymeric epoxide networks constitute a major class of thermosetting polymers and are extensively used as coatings, electronic materials, and adhesives (13). Owing to their outstanding mechanical and electrical properties, chemical resistance, adhesion, and minimal shrinkage after curing, they are used in structural applications as well.

Most of these thermoset types are industrially manufactured from bisphenol A (BPA), a substance that was initially synthesized as a chemical estrogen (13). The awareness of BPA toxicity combined with the limited availability and volatile cost of fossil resources and the non-recyclability of thermosets implies necessary changes in the field of epoxy networks. Thus, substitution of BPA has witnessed an increasing number of studies both from the academic and industrial

Compound	Reference
Epoxy crotyl sucrose	(14)
Ethylene oxide	(15)
Propylene oxide	(15)
1,2-Butylene oxide	(15)
2,3-Butylene oxide	(15)
2,3-Epoxy heptane	(15)
Nonene oxide	(15)
5-Butyl-3,4-epoxyoctane	(15)
1,2-Epoxy dodecane	(15)
1,2-Epoxy hexadecane	(15)
1,2-Epoxy octadecane	(15)
5-Benzyl-2,3-epoxy heptane	(15)
4-Cyclo-hexyl-2,3-epoxy pentane	(15)
Chlorostyrene oxide	(15)
Styrene oxide	(15)
<i>o</i> -Ethylstyrene oxide	(15)
<i>m</i> -Ethylstyrene oxide	(15)
<i>p</i> -Ethylstyrene oxide	(15)
Glycidyl benzene	(15)
7-Oxabicyclo[4.1.0]heptane	(15)
Oxabicyclo[3.1.0]hexane	(15)
4-Propyl-7-oxabicyclo[4.1.0]heptane	(15)
3-Amyl-6-oxabicyclo[3.1.0]hexane	(15)

 Table 1.4 Epoxide Monomers.



Epoxy crotylsucrose





2,3-Epoxy heptane



Styrene oxide



Propylene oxide



7-Oxabicyclo[4.1.0]heptane

1,2-Butylene oxide

Figure 1.5 Epoxide monomers.

sides. This review presents an overview of the reported aromatic multifunctional epoxide building blocks synthesized from biomass or from molecules that could be obtained from transformed biomass.

The main glycidylation routes and mechanisms and the BPA toxicity were described. Also, the main natural sources of aromatic molecules have been detailed. The various epoxy prepolymers can be organized into simple mono-aromatic di-epoxy, mono-aromatic poly-epoxy, and derivatives with numerous aromatic rings and epoxy groups (13).

1.1.3 Diol-Based Monomers

Diol-based monomers are presented in Table 1.5 and shown in Figure 1.6.

Compound	Compound
1,6-Hexanediol 1,10-Decanediol	1,8-Octanediol



Figure 1.6 Diol-based monomers.

The synthesis and characterization of variants of poly(diol fumarate) and poly(diol fumarate-*co*-succinate) were described. Through a Fischer esterification, α , ω -diols and dicarboxylic acids were polymerized to form aliphatic polyester comacromers. Because of the carbon-carbon double bond of fumaric acid, incorporating it into the macromer backbone structure resulted in unsaturated chains.

By choosing α , ω -diols of different lengths (1,6-hexanediol, 1,8-octanediol, and 1,10-decanediol) and controlling the amount of

fumaric acid in the dicarboxylic acid monomer feed (33, 50, and 100 mol%), nine diol-based macromer variants were synthesized and characterized for molecular weight, number of unsaturated bonds per chain, and thermal properties.

Degradation and *in vitro* cytotoxicity were also measured in a subset of macromers.

Macromer networks were photocrosslinked to demonstrate the ability to perform free radical addition using the unsaturated macromer backbone. Crosslinked macromer networks were also characterized for physicochemical properties (swelling, sol fraction, compressive modulus) based on diol length and amount of unsaturated bonds. A statistical model was built using data generated from these diol-based macromers and macromer networks to evaluate the impact of monomer inputs on final macromer and macromer network properties. With the ability to be modified by free radical addition, biodegradable unsaturated polyesters serve as important macromers in the design of devices such as drug delivery vehicles and tissue scaffolds. Given the ability to extensively control final macromer properties based on monomer input parameters, poly(diol fumarate) and poly(diol fumarate-*co*-succinate) represent an exciting new class of macromers (16).

1.1.4 Diacid-Based Monomers

Diacid-based monomers are shown in Table 1.6 and in Figure 1.7.

Compound	Compound
2,5-Furan dicarboxylic acid 2,3-Furan dicarboxylic acid Azelaic acid	3,4-Furan dicarboxylic acid Adipic acid

Table 1.6 Diacid based monomers.

1.1.5 Bio-based monomers

Bio-based platforms for polymers are shown in Table 1.8.

Also, the routes to some representative sustainable polymers that are synthesized from biomass feedstocks were



2,5-Furan dicarboxylic acid

Figure 1.7 Diacid based monomers.

Table 1.7 Bio-based monomers (17).
--------------------------------	------

Compound	Compound	Compound
Hydroxy acids Diamines Amino acids	Diacids Triglycerides	Diols Fatty acids

Table 1.8 Bio-Based Platforms (17).

Platform	Monomer type	Polymer type
Sugar	Hydroxy acids, diacids, diols, diamines, cyclics, vinyl	Copolyesters, polyester polyols, copolyamides, poly(urethane)s, polyolefins, polyacids
Lignin	Acids, alcohols	Polyesters, polybenzoxazines
CÕ ₂	Cyclic carbonates Polycarbonates, non-iso- cyanate poly(urethane)s	
Vegetable oils	Triglycerides, fatty acids	Polyesters, poly(urethane)s, thermosets
Proteins	Amino acids, (macro)cyclics	Poly(amino acid)s, poly(ester urea)s, polydepsipeptides, poly(ester amide ester)s, pep- toids, cationic polymers

shown (17). Natural biopolymers, including polysaccharides, lignin, lipids, polypeptides and terpenes, can be extracted from renewable biomass. Through deconstruction and conversion or fermentation, natural biopolymers can be turned into polymer precursors for sustainable polymerization. Sustainable polymers are poly(ethylene), poly(propylene), poly(ethylene 2,5-furandicarboxylate), poly(furfural alcohol), poly(hydroxyalkanoate)s, poly(lactide) and poly(butylene succinate).

The recent advances in the microbial production of diamines, aminocarboxylic acids, and diacids as potential platform chemicals and bio-based polyamides monomers have been described (18).

Bio-based manufacturing processes of chemicals and polymers in biorefineries using renewable resources have extensively been developed for the sustainable carbon dioxide (CO₂) neutral-based industry. Bio-based diamines, aminocarboxylic acids, and diacids have been used as monomers for the synthesis of polyamides with different carbon numbers and ubiquitous and versatile industrial polymers and also as precursors for further chemical and biological processes to afford valuable chemicals.

These platform biochemicals have been successfully produced by biorefinery processes employing enzymes and/or microbial host strains as main catalysts (18).

Metabolic engineering strategies of microbial consortia and optimization of microbial conversion processes, including whole cell bioconversion and direct fermentative production, have been developed.

1.1.6 Fatty Acids

Monomeric unsaturated fatty acids, which are derived from natural sources, are capable of being polymerized to the dimerized and trimerized form (19). This is usually realized by heating such unsaturated fatty acids in the presence of catalytic proportions of a mineral clay and, preferably, an acid-treated mineral clay, at temperatures in excess of about 180°C in an aqueous environment under autogenous pressure. Small amounts of water are deemed necessary for reaction to minimize the degradation of the fatty acids being treated (19).

12 FUTURE TRENDS IN MODERN PLASTICS

Fatty acid monomers can be employed as reactive diluents for the polymerization of vinyl esters and polyesters (20, 21). They can improve the fracture resistance, lower the processing viscosity and reduce the volatile organic compounds that are present in the polymerization mixture.

Fatty acid monomers can be used to replace some or all of the styrene used in liquid thermosetting resins. They are excellent alternatives to styrene because of their low cost and low volatility.

Furthermore, fatty acids are derived from plant oils, and are therefore a renewable resource. Thus, not only would the use of fatty acids in liquid molding resins reduce health and environmental risks, but it also promotes global sustainability. Fatty acids and triglycerides have been used in a number of polymeric applications (20, 21).

The preparation of epoxidized and hydroxylated fatty acids has been reviewed (22–24).

Fatty acids that may be employed to synthesize fatty acid monomers are listed in Table 1.9. Some of these compounds are shown in Figure 1.8

Compound	Compound	Compound
Butyric acid Lauric acid Stearic acid	Capric acid Myristic acid Oleic acid	Caprylic acid Palmitic acid Linoleic acid

Table 1.9 Fatty acids for fatty acidmonomers.

A polymeric composition, wherein the fatty acid monomer is a monomer of the formula, is shown in Figure 1.9.

Here, R is selected from the group consisting of a C_2 -- C_{30} saturated alkyl residue, an unsaturated alkyl residue, an acetylenic alkyl residue, a hydroxyl alkyl residue, a carboxylic acid alkyl residue, a divinyl ether alkyl residue, a sulfur-containing alkyl residue, an amide alkyl residue, a methoxy alkyl residue, a keto alkyl residue, a halogenated alkyl residue, a branched methoxy alkyl residue, a branched hydroxyl alkyl residue, an epoxy alkyl residue, a fatty acyl-CoA alkyl residue, a cyclopropane alkyl residue, a cyclopentenyl



Figure 1.8 Fatty acids.

alkyl residue, a cyclohexyl alkyl residue, a furanoid alkyl residue, a phenylalkanoic alkyl residue, and a lipoic alkyl residue (20, 21).



Figure 1.9 Fatty acid monomer.

1.1.7 Cyclic Fatty Acids

Cyclic fatty acid monomers have been found in frying oils used for fast foods (25).

Cyclic fatty acids can be classified into those that are naturally occurring and those that are formed in vegetable oils during heating (26). The former include cyclopropane, cyclopropene and cyclopentenyl acids. C17 and C19 cyclopropane acids are common in many bacteria, such as lactobacilli and enterobacteria; and mycolic (2-alkyl-3-hydroxy) acids, with up to about 90 carbons and one or two cyclopropane rings, occur in mycobacteria (27, 28).

Several acids with up to 26 carbons, one or two cyclopropane rings and a double bond in the 5 position were identified in an invertebrate from a deep-water lake (29). The C18 and C19 cyclopropane acids occur in varying amounts in the seed oils of some species of a few plant families, including Malvaceae and Sterculiaceae (27, 30). The cyclopropene counterparts are more widespread in these families, and cyclopentenyl acids are present in the seed oils of the family Flacourtiaceae, notably the genus *Hydnocarpus* (30).

Fatty acids with six-membered (31) and seven-membered rings have been characterized from the thermoacidophilic bacterium, *Bacillus acidocaldarius*.

1.1.8 Triglycerides

Epoxidized and acrylated triglycerides have been used as plasticizers and toughening agents (20, 21). In fact, the largest non-food use of triglycerides is the use of epoxidized soybean and linseed oils as plasticizers in poly(vinyl chloride). Epoxidized triglycerides have also been studied for their use as toughening agents in epoxy polymers.

The potential of epoxidized palm oil as plasticizer for poly(lactic acid) (PLA) was compared with commercialized epoxidized soybean oil (32). The plasticizers were melt-compounded into PLA at 3%, 5%, 10%, and 15%. As the aim was for the blends to be characterized towards packaging appropriate for food products, they were hot-pressed into 0.3 *mm* sheets, which is the approximate thickness of clamshell packaging. Fourier transform infrared spectroscopy confirmed the compatibility of the plasticizers with PLA. At similar loadings, epoxidized palm oil was superior in reinforcing elongation at break, thermal, and barrier properties of PLA.

The ductility of PLA was notably improved to 50.0% with the addition of 3% of epoxidized palm oil. From differential scanning calorimetry, the increase in crystallinity and the shifts in enthalpy of fusions in all plasticized blends denoted facilitation of PLA to form thermally stable α -form crystals.

The addition of epoxidized palm oil enabled PLA to become highly impermeable to oxygen, which can extend its potential in packaging an extensive range of oxygen-sensitive food (32).

1.1.9 Ester-Based Monomers

Some modern ester-based monomers are shown in Table 1.10.

The free-radical polymerization of dialkyl methylene malonate monomers using heat, UV light and peroxide has been described (33–35). Here, the monomer was prepared using traditional methods, which results in a monomer with low purity. The polymers are prepared via bulk polymerization. One would therefore not expect to be able to control polymer properties such as molecular weight and molecular weight distribution.

The polymerization of 1,1-disubstituted alkene compounds using anionic polymerization processes which are useful in the bulk polymerization of 1,1-disubstituted alkene compounds and processes which can operate at or near ambient conditions have been reported. Anionic bulk polymerizations may be initiated using a wide range of initiators, and may even be initiated by contact with certain substrates. Other bulk polymerization reactions may be ini-

Table 1.10 Ester-based monomers (35).

Compound	Compound
Methylene malonate	Dibutyl methylene malonate
Diethyl methylene malonate	Dihexyl methylene malonate
Dimethyl methylene malonate	Dipentyl methylene malonate
Butyl ethyl methylene malonate	Ethyl hexyl methylene malonate
Diisopropyl methylene malonate	Ethyl pentyl methylene malonate
Hexyl methyl methylene mal-	Butyl methyl methylene mal-
onate	onate
Diethoxyethyl methylene mal-	Dimethoxyethyl methylene mal-
onate	onate
Menthyl methyl methylene mal-	Methyl pentyl methylene mal-
onate	onate
Methyl propyl methylene mal-	Fenchyl methyl methylene mal-
onate	onate
Ethoxyethyl ethyl methylene malonate	Di-N-propyl methylene malonate
Ethyl methoxyethyl methylene malonate	Ethoxyethyl methyl methylene malonate
2-Phenylpropyl ethyl methylene malonate2-Phenyl-1-propanol ethyl methylene malonate	Methoxyethyl methyl methylene malonate