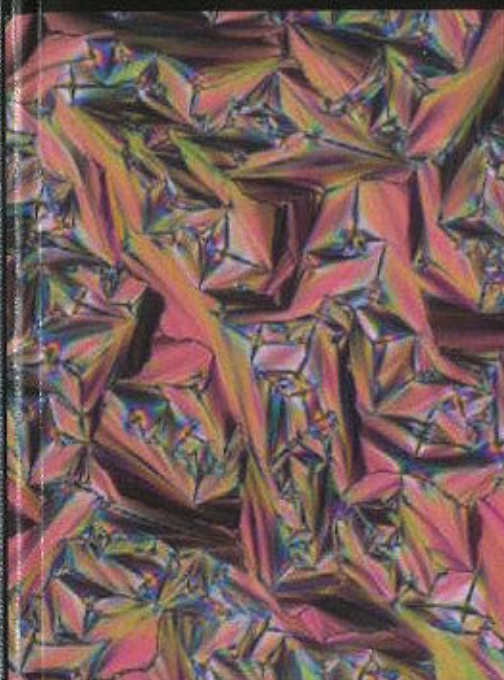
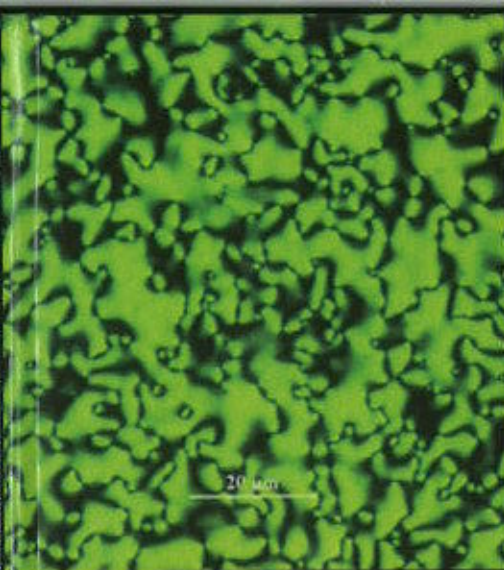




SECOND EDITION

HANDBOOK OF THERMOPLASTICS

EDITED BY

Olagoke Olabisi
Kolapo Adewale

 **CRC Press**
Taylor & Francis Group

SECOND
EDITION

HANDBOOK OF THERMOPLASTICS

CBN BRNCH
GenColl

TP 1180
.T5 H36
2016
Copy 1



ITEM MAY BE REMOVED FROM THE LIBRARY OF CONGRESS

Patron: Cooley LLP
Patron Group: ILL-US
Final Due Date: 8/8/2022 05:00 AM
Title: Handbook of thermoplastics / edited by Olagoke Olabisi, Kolapo Adewale.
Author:
Call Number: TP1180.T5 H36 2016 CABIN BRANCH
Enumeration:
Chronology:
Copy: 1
Item Barcode: *00405215986*

THIS CARD MUST BE RETURNED WITH ITEM. Please note Final Due Date above. Your borrowing privileges may be suspended if this item has not been checked in by that date. This item may be removed from the Library of Congress. However, this item is not authorized to leave the borrowing library's premises.

ITEM MAY BE REMOVED FROM THE LIBRARY OF CONGRESS

Patron: Cooley LLP
Patron Group: ILL-US
Final Due Date: 8/8/2022 05:00 AM
Title: Handbook of thermoplastics / edited by Olagoke Olabisi, Kolapo Adewale.
Author:
Call Number: TP1180.T5 H36 2016 CABIN BRANCH
Enumeration:
Chronology:
Copy: 1
Item Barcode: *00405215986*

THIS CARD MUST BE RETURNED WITH ITEM. Please note Final Due Date above. Your borrowing privileges may be suspended if this item has not been checked in by that date. This item may be removed from the Library of Congress. However, this item is not authorized to leave the borrowing library's premises.

LIBRARY OF
CONGRESS



SECOND EDITION

HANDBOOK OF THERMOPLASTICS

SECOND EDITION

HANDBOOK OF THERMOPLASTICS

EDITED BY

**Olagoke Olabisi
Kolapo Adewale**



CRC Press

Taylor & Francis Group
Boca Raton London New York

CRC Press is an imprint of the
Taylor & Francis Group, an **informa** business

CRC Press
Taylor & Francis Group
6000 Broken Sound Parkway NW, Suite 300
Boca Raton, FL 33487-2742

© 2016 by Taylor & Francis Group, LLC
CRC Press is an imprint of Taylor & Francis Group, an Informa business

No claim to original U.S. Government works

Printed on acid-free paper
Version Date: 20151007

International Standard Book Number-13: 978-1-4665-7722-0 (Hardback)

This book contains information obtained from authentic and highly regarded sources. Reasonable efforts have been made to publish reliable data and information, but the author and publisher cannot assume responsibility for the validity of all materials or the consequences of their use. The authors and publishers have attempted to trace the copyright holders of all material reproduced in this publication and apologize to copyright holders if permission to publish in this form has not been obtained. If any copyright material has not been acknowledged please write and let us know so we may rectify in any future reprint.

Except as permitted under U.S. Copyright Law, no part of this book may be reprinted, reproduced, transmitted, or utilized in any form by any electronic, mechanical, or other means, now known or hereafter invented, including photocopying, microfilming, and recording, or in any information storage or retrieval system, without written permission from the publishers.

For permission to photocopy or use material electronically from this work, please access www.copyright.com (<http://www.copyright.com/>) or contact the Copyright Clearance Center, Inc. (CCC), 222 Rosewood Drive, Danvers, MA 01923, 978-750-8400. CCC is a not-for-profit organization that provides licenses and registration for a variety of users. For organizations that have been granted a photocopy license by the CCC, a separate system of payment has been arranged.

Trademark Notice: Product or corporate names may be trademarks or registered trademarks, and are used only for identification and explanation without intent to infringe.

Visit the Taylor & Francis Web site at
<http://www.taylorandfrancis.com>

and the CRC Press Web site at
<http://www.crcpress.com>

*To our children—Lara Olabisi, Simi Olabisi, Wande Olabisi, Toyosi Olabisi,
Banji Olabisi, Lanre Olabisi, Dr. Ronke Olabisi, Toke Olabisi,
and Bunmi Olabisi; Tomi Adewale, Funmi Adewale, and Isaac Adewale*

able efforts have been
onsibility for the valid-
d to trace the copyright
ission to publish in this
d let us know so we may

ced, transmitted, or uti-
d, including photocopy-
ten permission from the

w.copyright.com ([http://](http://www.copyright.com)
ive, Danvers, MA 01923,
r a variety of users. For
ment has been arranged.

s, and are used only for

Contents

Preface.....	xi
Editors.....	xiii
Contributors	xv
Chapter 1 Polyolefins	1
<i>Olagoke Olabisi</i>	
Chapter 2 Vinyl Alcohol Polymers	53
<i>Kereilemang Khana Mokwena Nthoiwa, Carlos A. Diaz, and Yash Chaudhari</i>	
Chapter 3 Polyvinyl Butyral	89
<i>Christian Carrot, Amine Bendaoud, and Caroline Pillon</i>	
Chapter 4 Polyacrylonitrile	139
<i>Johannis C. Simitzis and Spyridon K. Soulis</i>	
Chapter 5 Polyacrylates.....	169
<i>Joke Vandenbergh and Thomas Junkers</i>	
Chapter 6 Polyacetals.....	193
<i>Kinga Pielichowska</i>	
Chapter 7 Polyethers	251
<i>Rebecca Klein and Frederik R. Wurm</i>	
Chapter 8 Aromatic Polyamides	285
<i>Miriam Trigo, Jesús L. Pablos, Félix C. García, and José M. García</i>	
Chapter 9 Thermoplastic Polyesters.....	319
<i>Ganesh Kannan, Sarah E. Grieshaber, and Wei Zhao</i>	
Chapter 10 Polycarbonates.....	347
<i>Pierre Moulinié</i>	
Chapter 11 Liquid Crystalline Polymers	369
<i>Xiao Li and Haifeng Yu</i>	

Chapter 12 Thermoplastic Polyurethanes.....	387
<i>Koh-Hei Nitta and Mizue Kuriyagawa</i>	
Chapter 13 Fluoroplastics	397
<i>Thierry A. Blanchet</i>	
Chapter 14 Polyarylethersulfones	419
<i>M. Jamal El-Hibri and Shari W. Axelrad</i>	
Chapter 15 Ketone-Based Thermoplastics.....	461
<i>Yundong Wang and Mukerrem Cakmak</i>	
Chapter 16 Polyimides	491
<i>Hooman Abbasi, Marcelo Antunes, and José Ignacio Velasco</i>	
Chapter 17 Polyphenylquinoxalines	533
<i>Jin-Gang Liu</i>	
Chapter 18 Aromatic Polyhydrazides and Their Corresponding Polyoxadiazoles.....	571
<i>Emilia Di Pace, Paola Laurienzo, Mario Malinconico, and Maria Grazia Volpe</i>	
Chapter 19 Polybenzimidazoles.....	617
<i>Yan Wang, Tingxu Yang, Kayley Fishel, Brian C. Benicewicz, and Tai-Shung Chung</i>	
Chapter 20 Conductive Thermoplastics	669
<i>Louis M. Leung</i>	
Chapter 21 Advanced Thermoplastic Composites.....	693
<i>Salvatore Iannace, Gianfranco Carotenuto, Luigi Sorrentino, Mariano Palomba, and Luigi Nicolais</i>	
Chapter 22 Natural Fiber Thermoplastic Composites	727
<i>Norma E. Marcovich, María M. Reboredo, and Mirta I. Aranguren</i>	
Chapter 23 Material Selection, Design, and Application	753
<i>Eungkyu Kim, Patrick Lee, Joe Dooley, and Mark A. Barger</i>	

.....	387
.....	397
.....	419
.....	461
.....	491
.....	533
.....	571
.....	617
.....	669
.....	693
.....	727
n	753

Chapter 24	Laser Processing of Thermoplastic Composites	805
	<i>Peter Jaeschke and Verena Wippo</i>	
Chapter 25	Bioplastics	835
	<i>Caisa Johansson</i>	
Chapter 26	Thermoplastic Additives: Flame Retardants.....	877
	<i>Kolapo Peluola Adewale</i>	
Chapter 27	Recycling of Thermoplastics.....	919
	<i>Jesús María García-Martínez and Emilia P. Collar</i>	
Chapter 28	Environment Health and Safety: Regulatory and Legislative Issues	941
	<i>Emilia P. Collar and Jesús María García-Martínez</i>	
Index		957

9 Thermoplastic Polyesters*

Ganesh Kannan, Sarah E. Grieshaber, and Wei Zhao

CONTENTS

9.1	Poly(Ethylene Terephthalate).....	320
9.1.1	History	320
9.1.2	PET Polymerization Process	320
9.1.2.1	Antimony	320
9.1.2.2	Germanium	320
9.1.2.3	Other PET Catalysts.....	320
9.1.2.4	PET Synthesis	321
9.1.2.5	Solid-State Polymerization	321
9.1.3	Properties and Applications of PET	322
9.2	Poly(Butylene Terephthalate).....	324
9.2.1	History	324
9.2.2	Raw Materials.....	324
9.2.3	PBT Polymerization Process	327
9.2.4	Green Chemistry	329
9.2.5	PBT Crystallization	329
9.2.6	PBT Properties and Applications	329
9.3	Polyesters Based on Cyclohexanedimethanol	331
9.3.1	History of CHDM-Based Polyesters.....	331
9.3.2	Polymerization Process.....	332
9.3.3	Properties and Applications.....	334
9.4	Naphthalate Polyesters.....	336
9.4.1	History	336
9.4.2	Polymerization Process.....	337
9.4.3	Thermal Properties of Naphthalate Polyesters	337
9.4.4	Gas Permeability	338
9.4.4.1	Gas Barrier Properties of PEN/PET Blends	339
9.4.5	Chemical Resistance.....	339
9.4.6	Optical (UV) Properties	339
9.4.7	Fluorescence of Naphthalate Polyesters	340
9.4.8	Photodegradation.....	340
9.4.9	Mechanical Properties	340
9.4.10	Naphthalate-Based Elastomers	340
9.4.11	Applications	341
	References.....	342

* Based in parts on the first-edition chapter on thermoplastic polyesters.

9.1 POLY(ETHYLENE TEREPHTHALATE)

9.1.1 HISTORY

Calico Printer's Association Limited initiated research in 1940 to develop polyesters for synthetic fiber applications. In 1941, John Rex Whinfield and James Tennant Dickson of the Calico Printer's Association patented poly(ethylene terephthalate) (PET) [1] based on the early research of Wallace Carothers on condensation polymerization of aliphatic acids such as adipic acid with ethylene glycol (EG), but Carothers had not studied the condensation of EG with aromatic acids such as terephthalic acid (TPA) to produce PET. Whinfield and Dickson, along with inventors W.K. Birtwhistle and C.G. Ritchie, also created the first PET polyester fibers called Terylene in 1941 [2] (first manufactured by Imperial Chemical Industries [ICI]). When DuPont learned about the new fibers from ICI (which acquired Calico industries in 1947), it negotiated and purchased patent rights and then proceeded further to commercialization.

9.1.2 PET POLYMERIZATION PROCESS

Until the mid-1960s, dimethyl terephthalate (DMT) was the preferred feedstock for PET production, mainly due to its higher purity than its acid form, TPA. When Amoco developed a high-purity TPA process, the acid form gained acceptance and has since become the primary feedstock. The acid process completely eliminated the additional step of converting TPA to dimethyl ester, which added further cost, and this was also an important criterion for the worldwide acceptance of TPA-based PET. Owing to the commercial importance of PET, large volumes of work on various catalysts used for PET polymerization have been reported, and a detailed discussion on the catalysts follows.

The metal catalysts based on antimony and germanium have dominated the industrial production process from the time of invention. Since PET has gained commercial importance from 1950 onward, new research has been focused on improving the process, especially the catalysts, both inorganic and organic. Although a plethora of new catalysts were discovered, replacement of antimony and germanium as industrial-scale catalysts has not succeeded to date. So far, no negative data have been obtained due to the presence of antimony in PET sold for food applications.

9.1.2.1 Antimony

Among the various antimony compounds such as trioxide [3], triacetate [4], and glycolate [5], the most widely used industrial version is the trioxide. The other two catalysts do not show any significant difference from PET synthesized with antimony trioxide.

9.1.2.2 Germanium

Germanium dioxide-catalyzed [6] PET shows higher optical clarity, resulting in its use in film applications. It is also used by Japanese producers for manufacturing bottle-grade PET. Because of its tendency to support oxidative degradation, germanium catalysts are used together with stabilizers based on phosphorus.

9.1.2.3 Other PET Catalysts

Due to the commercial importance of PET, an abundance of patents focusing on either new catalyst or combinations of existing catalysts have been reported, a few of which are described. Examples of mixture catalysts include zinc acetate/antimony acetate/phosphate ester [7], manganese benzoate/antimony triacetate/phosphate ester [7], manganese benzoate/acetyltriisopropyl titanate with or without cobalt acetate [7], antimony triacetate/zinc diacetate/titanium glycolate [8], and manganese acetate/cobalt acetate/antimony trioxide/titanium isopropoxide [9]. Examples of other novel compounds include triethanolamine titanium chelate [10]; titanium glycolate [8]; cyanides of calcium, cadmium, or zinc (for PET prepolymer) [11]; cobalt acetate [12]; stannous formate [13]; acetylacetonates of manganese, cobalt, cadmium, zinc, or magnesium [14]; phenylstibonic acid [15]; *p*-chlorophenylstibinic acid [15];

polyesters for synthetic
of the Calico Printer's
research of Wallace
with ethylene glycol
s such as terephthalic
W.K. Birtwhistle and
1941 [2] (first manu-
the new fibers from
patent rights and then

work for PET production,
ed a high-purity TPA
y feedstock. The acid
yl ester, which added
ptance of TPA-based
various catalysts used
catalysts follows.
the industrial produc-
importance from 1950
ly the catalysts, both
, replacement of anti-
e. So far, no negative
l applications.

and glycolate [5], the
not show any signifi-

in its use in film appli-
e PET. Because of its
together with stabilizers

n either new catalyst or
bed. Examples of mix-
ese benzoate/antimony
with or without cobalt
nganese acetate/cobalt
el compounds include
um, cadmium, or zinc
tonates of manganese,
henylstibinic acid [15];

cobalt tungstate [16]; lead oxide [17]; lead fluoride [18]; trifluoroacetates of manganese, magnesium, or calcium [19]; and perfluorobutyrate of barium, tin, or calcium [19]. Regarding metal-free organic catalysts for PET synthesis, an example can be found using *N*-heterocyclic carbene as a catalyst [20]. The above-mentioned examples are by no means exhaustive, as the literature has been flooded with several catalysts, and our effort is to provide a brief understanding of various catalyst approaches that have been reported.

The majority of efforts in developing new catalysts are focused on finding a substitute for antimony. However, until a regulatory demand for antimony-free PET is put into effect, antimony will continue to be the main catalyst used commercially.

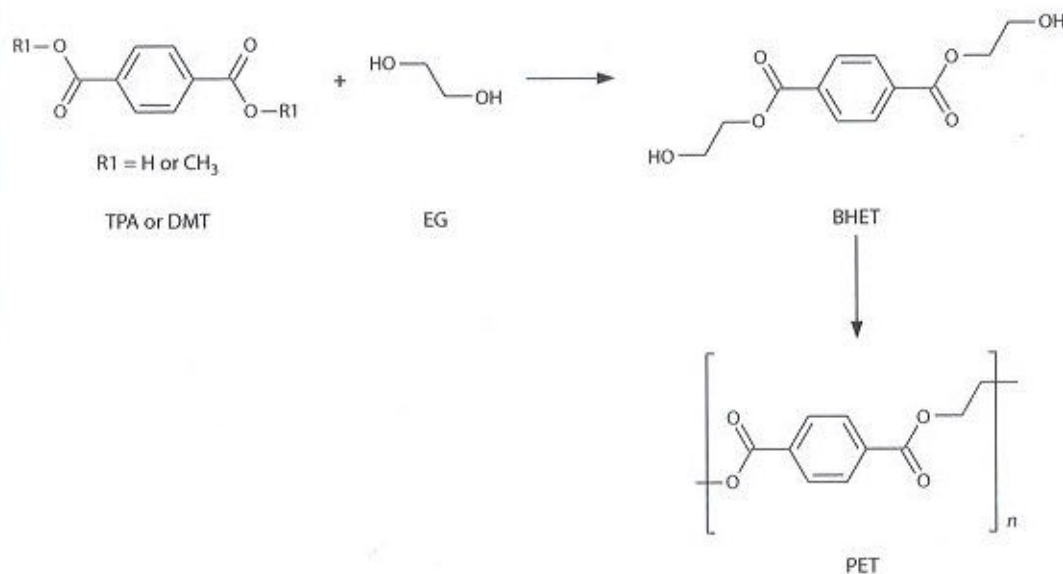
9.1.2.4 PET Synthesis

PET is synthesized from EG as the diol and either an acid (TPA) or an ester (DMT) (Scheme 9.1). Unlike typical condensation polymerization, which requires equal stoichiometric (1:1) amounts of acid and alcohol, EG is typically charged in excess to the acid [7]. During the first stage of polymerization, the intermediate bis-(2-hydroxyethyl)-terephthalate (BHET) monomer is produced and further polymerized under reduced pressure with heat to produce PET resin [21], as shown in Scheme 9.1.

The final molecular weight is influenced by factors such as time, temperature, and vacuum. Typically, the polymerization temperature is increased gradually in the range of 200–290°C, and the melt polymerization time can be in the range of 2–5 h. DMT reacts faster than TPA due to its lower melting point (142°C). Although DMT was initially used commercially, TPA is currently the monomer of choice for PET production.

9.1.2.5 Solid-State Polymerization

As mentioned earlier, one of the factors that influence the molecular weight is the polymerization time. In order to get very high molecular weights, the polymerization time has to be significantly longer. As the polymer melt resides for a longer time at a very high temperature, the polymer often develops a brown color due to thermal degradation. Commercially, the requirement is not only higher molecular weight but also no color formation. Films and fibers are made by melt-phase polymerization until intrinsic viscosities (IVs) of 0.5–0.7 dL/g are reached. Above 0.7 dL/g (soft drink and beverage bottles, tire cord filaments, and industrial fibers), the solid-state polymerization



SCHEME 9.1 PET manufacturing route.

9.1 POLY(ETHYLENE TEREPHTHALATE)

9.1.1 HISTORY

Calico Printer's Association Limited initiated research in 1940 to develop polyesters for synthetic fiber applications. In 1941, John Rex Whinfield and James Tennant Dickson of the Calico Printer's Association patented poly(ethylene terephthalate) (PET) [1] based on the early research of Wallace Carothers on condensation polymerization of aliphatic acids such as adipic acid with ethylene glycol (EG), but Carothers had not studied the condensation of EG with aromatic acids such as terephthalic acid (TPA) to produce PET. Whinfield and Dickson, along with inventors W.K. Birtwhistle and C.G. Ritchie, also created the first PET polyester fibers called Terylene in 1941 [2] (first manufactured by Imperial Chemical Industries [ICI]). When DuPont learned about the new fibers from ICI (which acquired Calico industries in 1947), it negotiated and purchased patent rights and then proceeded further to commercialization.

9.1.2 PET POLYMERIZATION PROCESS

Until the mid-1960s, dimethyl terephthalate (DMT) was the preferred feedstock for PET production, mainly due to its higher purity than its acid form, TPA. When Amoco developed a high-purity TPA process, the acid form gained acceptance and has since become the primary feedstock. The acid process completely eliminated the additional step of converting TPA to dimethyl ester, which added further cost, and this was also an important criterion for the worldwide acceptance of TPA-based PET. Owing to the commercial importance of PET, large volumes of work on various catalysts used for PET polymerization have been reported, and a detailed discussion on the catalysts follows.

The metal catalysts based on antimony and germanium have dominated the industrial production process from the time of invention. Since PET has gained commercial importance from 1950 onward, new research has been focused on improving the process, especially the catalysts, both inorganic and organic. Although a plethora of new catalysts were discovered, replacement of antimony and germanium as industrial-scale catalysts has not succeeded to date. So far, no negative data have been obtained due to the presence of antimony in PET sold for food applications.

9.1.2.1 Antimony

Among the various antimony compounds such as trioxide [3], triacetate [4], and glycolate [5], the most widely used industrial version is the trioxide. The other two catalysts do not show any significant difference from PET synthesized with antimony trioxide.

9.1.2.2 Germanium

Germanium dioxide-catalyzed [6] PET shows higher optical clarity, resulting in its use in film applications. It is also used by Japanese producers for manufacturing bottle-grade PET. Because of its tendency to support oxidative degradation, germanium catalysts are used together with stabilizers based on phosphorus.

9.1.2.3 Other PET Catalysts

Due to the commercial importance of PET, an abundance of patents focusing on either new catalyst or combinations of existing catalysts have been reported, a few of which are described. Examples of mixture catalysts include zinc acetate/antimony acetate/phosphate ester [7], manganese benzoate/antimony triacetate/phosphate ester [7], manganese benzoate/acetyltriisopropyl titanate with or without cobalt acetate [7], antimony triacetate/zinc diacetate/titanium glycolate [8], and manganese acetate/cobalt acetate/antimony trioxide/titanium isopropoxide [9]. Examples of other novel compounds include triethanolamine titanium chelate [10]; titanium glycolate [8]; cyanides of calcium, cadmium, or zinc (for PET prepolymer) [11]; cobalt acetate [12]; stannous formate [13]; acetylacetonates of manganese, cobalt, cadmium, zinc, or magnesium [14]; phenylstibonic acid [15]; *p*-chlorophenylstibonic acid [15];

polyesters for synthetic of the Calico Printer's y research of Wallace d with ethylene glycol ds such as terephthalic W.K. Birtwhistle and n 1941 [2] (first manu- at the new fibers from patent rights and then

ck for PET production, ped a high-purity TPA y feedstock. The acid hyl ester, which added eptance of TPA-based various catalysts used catalysts follows. the industrial produc- mportance from 1950 lly the catalysts, both l, replacement of anti- e. So far, no negative d applications.

and glycolate [5], the o not show any signifi-

in its use in film appli- le PET. Because of its gether with stabilizers

n either new catalyst or ibed. Examples of mix- ese benzoate/antimony with or without cobalt anganese acetate/cobalt el compounds include ium, cadmium, or zinc etonates of manganese, phenylstibinic acid [15];

cobalt tungstate [16]; lead oxide [17]; lead fluoride [18]; trifluoroacetates of manganese, magnesium, or calcium [19]; and perfluorobutyrate of barium, tin, or calcium [19]. Regarding metal-free organic catalysts for PET synthesis, an example can be found using *N*-heterocyclic carbene as a catalyst [20]. The above-mentioned examples are by no means exhaustive, as the literature has been flooded with several catalysts, and our effort is to provide a brief understanding of various catalyst approaches that have been reported.

The majority of efforts in developing new catalysts are focused on finding a substitute for antimony. However, until a regulatory demand for antimony-free PET is put into effect, antimony will continue to be the main catalyst used commercially.

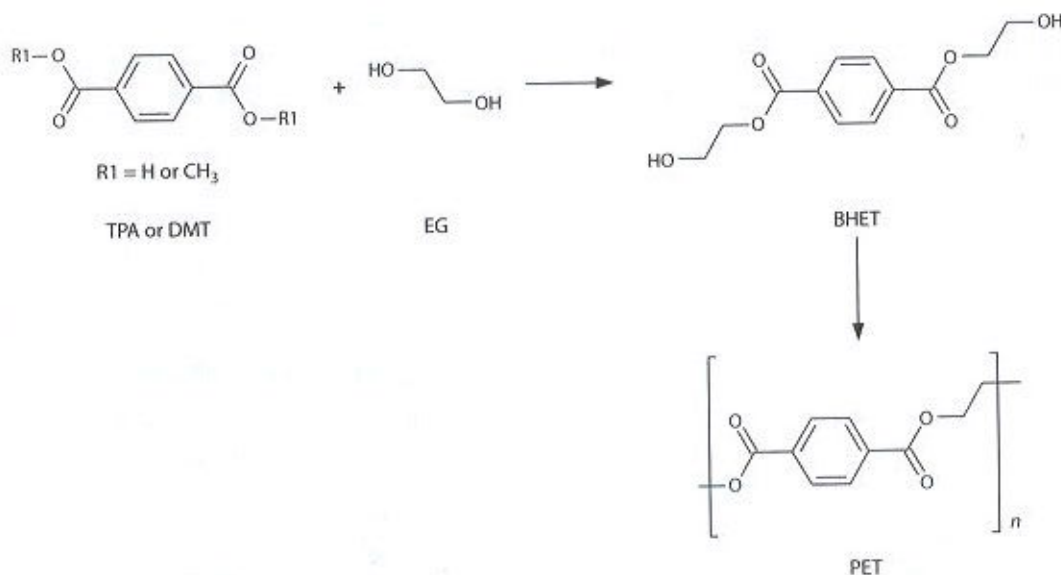
9.1.2.4 PET Synthesis

PET is synthesized from EG as the diol and either an acid (TPA) or an ester (DMT) (Scheme 9.1). Unlike typical condensation polymerization, which requires equal stoichiometric (1:1) amounts of acid and alcohol, EG is typically charged in excess to the acid [7]. During the first stage of polymerization, the intermediate bis-(2-hydroxyethyl)-terephthalate (BHET) monomer is produced and further polymerized under reduced pressure with heat to produce PET resin [21], as shown in Scheme 9.1.

The final molecular weight is influenced by factors such as time, temperature, and vacuum. Typically, the polymerization temperature is increased gradually in the range of 200–290°C, and the melt polymerization time can be in the range of 2–5 h. DMT reacts faster than TPA due to its lower melting point (142°C). Although DMT was initially used commercially, TPA is currently the monomer of choice for PET production.

9.1.2.5 Solid-State Polymerization

As mentioned earlier, one of the factors that influence the molecular weight is the polymerization time. In order to get very high molecular weights, the polymerization time has to be significantly longer. As the polymer melt resides for a longer time at a very high temperature, the polymer often develops a brown color due to thermal degradation. Commercially, the requirement is not only higher molecular weight but also no color formation. Films and fibers are made by melt-phase polymerization until intrinsic viscosities (IVs) of 0.5–0.7 dL/g are reached. Above 0.7 dL/g (soft drink and beverage bottles, tire cord filaments, and industrial fibers), the solid-state polymerization



SCHEME 9.1 PET manufacturing route.

(SSP) procedure is used by heating a low-molecular-weight PET below its melting point (245°C) but above its glass transition temperature (80°C) [22]. Between the melting point and glass transition, with heating, the polymerization continues, albeit at a slower rate, but ensures that no color bodies are formed. The ideal temperature range for SSP is 200–220°C. Vacuum or inert gas inside the SSP chamber ensures the removal of EG, water, and acetaldehyde [22].

The main mechanism for SSP is the diffusion of end groups (acid [or ester] and alcohol) and joining of the two chains with the elimination of by-products such as water (or methanol). Since the crystalline phase is highly ordered and possible movements are negligible, most of the reaction occurs in the amorphous domain [23]. Additionally, since the end group produces defects in the crystallites, most of the end groups are essentially in the amorphous phase, resulting in polymerization driven by the amorphous state [23]. Similar to melt polymerization, removal of water (or methanol) after the condensation by inert gas or vacuum drives the reaction forward.

9.1.3 PROPERTIES AND APPLICATIONS OF PET

Fully annealed PET has a melting point of 280°C, but commercial PET has lower crystallinity, and the melting point is between 255°C and 265°C [24]. The reason for the low crystallinity of commercial PET is both defects in the backbone generated by chemical impurities (diethylene glycol produced from EG) during polymerization becoming a part of the PET backbone [24], or deliberately added chemicals such as isophthalic acid (IPA) that improve processability and lower the crystallization rate. The addition of IPA to PET improves the melt strength that is required for bottle applications [25]. Typical properties of PET collected from data sheets are given in Table 9.1.

Due to the short $-\text{CH}_2-\text{CH}_2-$ spacer between the aromatic rings, PET crystallizes slowly, but the crystallization rate and, subsequently, the crystallinity in PET can be strongly influenced by the molecular weight. Low molecular weight allows the chain to align easily compared to higher molecular weight, resulting in higher crystallinity for the low-molecular-weight grades. A combination of molecular weight and crystallinity influences the final mechanical properties of a particular grade. For example, yield strain differs with both crystallinity as well as molecular weight [26], as shown in Table 9.2.

PET is flammable and requires flame-retardant additives for applications needing flame-retardant performance. The limiting oxygen index (LOI) for PET is approximately 21 [27], which means oxygen from air can support combustion. PET does not produce char while burning, which leads to complete combustion. Additives to make flame-retardant PET products are mostly halogen based

TABLE 9.1
Typical Properties of PET

Property	Unit	Value
Glass transition temperature	°C	80–82
Melting temperature	°C	245–265
Heat of fusion	J/g	104
Coefficient of thermal expansion	10^{-6} K^{-1}	20–80
Heat deflection temperature (0.45 MPa load)	°C	115
Specific gravity (amorphous)	–	1.33
Specific gravity (crystalline)	–	1.39
Tensile strength	MPa	55–75
Tensile modulus	GPa	2–4
Elongation at break	%	50–165
Izod impact strength (notched, 23°C)	J/m	13–35

melting point (245°C) but
ent and glass transition,
es that no color bodies
ert gas inside the SSP

ster] and alcohol) and
r (or methanol). Since
e, most of the reaction
roduces defects in the
resulting in polymer-
removal of water (or
forward.

as lower crystallinity,
e low crystallinity of
mpurities (diethylene
PET backbone [24],
ve processability and
melt strength that is
from data sheets are

crystallizes slowly, but
strongly influenced by
y compared to higher
ht grades. A combina-
properties of a particular
ecular weight [26], as

eding flame-retardant
[27], which means oxy-
urning, which leads to
mostly halogen based

Value

80-82

245-265

104

20-80

115

1.33

1.39

55-75

2-4

50-165

13-35

TABLE 9.2

Yield Strain (%) at 23°C [26] for Amorphous and Crystalline
PET Grades of Different Molecular Weights

IV of PET	Yield Strain (%)	
	Amorphous PET	PET with 40% Crystallinity
0.62	6.7	8.9
0.68	5.7	7.9
0.75	6.0	8.3
0.86	5.7	7.9

Source: Dixon, E.R. and Jackson, J.B., *J. Mater. Sci.*, 3:464, 1968.

such as brominated polystyrene [28] along with antimony (sodium antimonate) as a synergist, or phosphorous-based additives [28]. For phosphorus compounds, although phosphates provide good flame retardancy, the PET molecular weight decreases due to the hydrolysis by phosphoric acid, which is generated from the phosphate. On the other hand, red phosphorous provides excellent flame resistance but generates highly toxic phosphine [29] while burning.

Similar to most of the commercial polymers, PET is an insulator, which allows for applications such as electrical connectors.

The crystallinity of PET results in good resistance to most acids, alkalis, alcohols, greases, and oils. Since the barrier to gases is generally related to the free volume of the polymer, crystalline polymers provide excellent barrier properties because of the close packing of molecular chains. PET has been approved for food contact applications and is generally considered very safe to use. All the soda bottles in the world are made from PET as well as most of the drinking water bottles.

PET does not have weathering performance at the level of aliphatic polymers such as polyethylene and aliphatic nylons, but its weatherability is acceptable for most short- to medium-term applications.

Optically, PET has very high clarity and transmittance, depending on the processing conditions used. The slow crystallization rate of PET means that any process with fast cooling results in a clear product (bottles, films, sheets, etc.). Processes with a longer residence time or annealing at high temperatures cause PET to crystallize, which results in opaque products.

Among the commercial polyesters, PET is the most commonly used material not only due to its excellent properties but also because it has the lowest cost compared to other engineering thermoplastic polyesters. Similar to nylons and polycarbonates (PCs), drying of polyester (including PET) pellets in an oven at an ambient temperature for several hours is important to prevent polymer degradation by moisture during processing. Several different grades (differentiated by IV) of PET are made by the industry for various processing methods and final products. A few of the most common applications are also listed in Table 9.3.

TABLE 9.3

Grades of PET/Processing Type/Applications

Grade (IV dL/g)	Processing	Applications
0.68	Injection molding	Cups, connectors
0.76	Blow molding, film extrusion, fiber spinning	Bottles for mineral water, containers, cast film, fiber
0.8	Blow molding	General bottle applications
0.84	Blow molding, thermoforming	Bottles for carbonated drinks, juices, oils, cosmetics and food
0.9	Blow molding	4-5 gal. bottles, detergent bottles, jars, deep-draw cups

The advantage of low cost combined with crystallinity and higher thermal stability will continue to be the main reason for PET to be considered as the first material of choice for any new application and uniquely positioned to expand into new markets in the future. New inventions in processing and molding technologies will open new vistas for PET that have not yet been explored.

9.2 POLY(BUTYLENE TEREPHTHALATE)

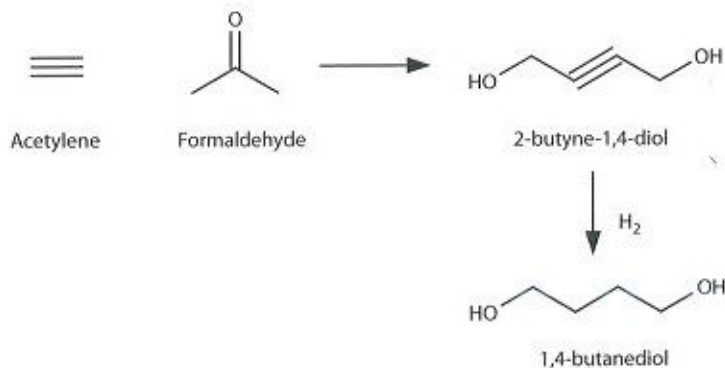
In addition to PET, poly(butylene terephthalate) (PBT) shares the designation of the most commercially significant thermoplastic polyester. According to a BCC market report, the global market of PET in 2012 was around 270,000 t, while the market size of PBT in 2012 was about 950,000 t [30]. The markets for both PET and PBT are projected to grow continuously in the coming years. Unlike PET, for which the major applications are fibers, films, and bottles, the main application for PBT is injection-molded parts, for which most utilize glass-filled or mineral-filled PBT. The butylene group in the PBT backbone provides the polymer with higher chain mobility than the ethylene group in the PET backbone and results in a faster crystallization speed. Faster crystallization makes PBT more suitable than PET for injection-molding processes [31].

9.2.1 HISTORY

The history of PBT dates back to the 1940s and is mingled with the history of PET. The theory of the stepwise growth process was documented by Carothers in the late 1920s, but it is difficult to unambiguously determine the inventor of PBT. Its commercialization began in the late 1960s with the first introduction of Calenex 3300, a 30% glass fiber-reinforced PBT injection-molding grade, by Ticona (now Celanese group) [32]. PBT neat resins, filled PBT grades, and blends of PBT are often found in automotive applications, home appliances, electrical and electronic devices, and other engineering thermoplastic parts due to their high flow characteristics, chemical resistance, thermal and mechanical properties, dimensional stability, and colorability.

9.2.2 RAW MATERIALS

The production of PBT generally starts from two raw materials: 1,4-butanediol (BDO) and DMT or TPA. BDO can be synthesized from various raw materials using different processes. For example, Reppe chemistry (shown in Scheme 9.2) is a process that uses acetylene and formaldehyde to produce 1,4-butyne-1,4-diol, which is then hydrogenated to obtain BDO. Reppe chemistry was invented in the 1930s [33] and is still a widely used route to produce BDO in industry. The Reppe reaction takes place using a catalyst based on copper oxide with bismuth oxide added [34]. And the synthesis in a



SCHEME 9.2 Reppe chemistry to produce BDO.

stability will continue for any new applications in processing and colored.

of the most commercial, the global market of is about 950,000 t [30]. In coming years. Unlike application for PBT is T. The butylene group the ethylene group in the tion makes PBT more

of PET. The theory
20s, but it is difficult
gan in the late 1960s
BT injection-molding
es, and blends of PBT
electronic devices, and
chemical resistance,

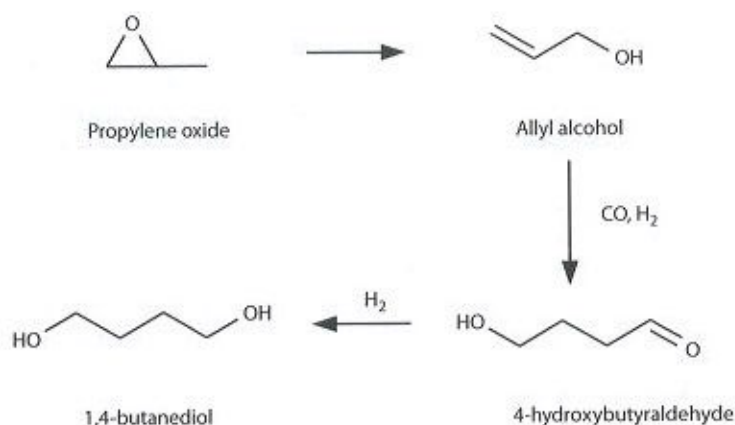
ol (BDO) and DMT or processes. For example, formaldehyde to pro-nistry was invented in the Reppe reaction takes And the synthesis in a

 —OH OH

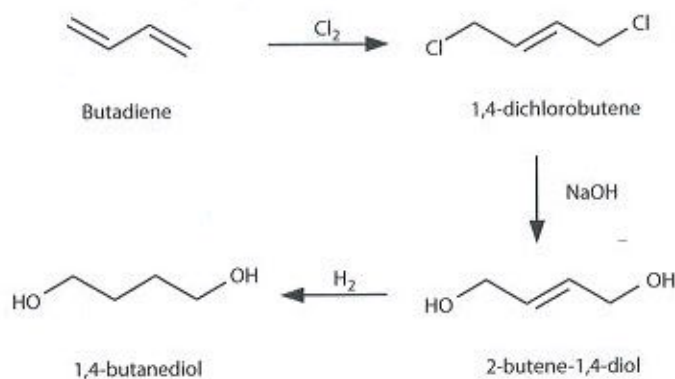
fluid bed reactor system happens at 70–100°C, 1–6 bar [35–37]. The pH of the reaction is controlled at 5–8 by the addition of alkali [35–37]. The hydrogenation of 1,4-butyndiol can be completed with a nickel or palladium catalyst.

Other feedstocks for the synthesis of BDO include propylene oxide (Scheme 9.3) [34,38,39], butadiene (Scheme 9.4) [34,38,40], and maleic anhydride (Scheme 9.5) [34,38,41].

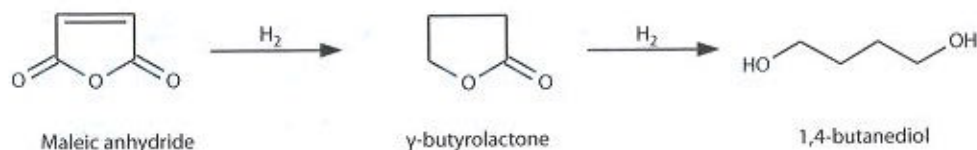
Recently, many companies have been developing bio-based routes for chemical synthesis due to the increasing price of oil and a broader awareness of sustainability, and consequently, bio-based BDO is gaining momentum in industry. Genomatica has developed and patented a one-step process to produce BDO through fermentation using non-naturally occurring microbial organisms [42], which is called the GENO BDO process. In late 2012, Genomatica and DuPont Tate & Lyle Bio Products Company, LLC, successfully produced over 2000 t of BDO through direct fermentation in a 5-week campaign, which was announced as “the first successful commercial-scale production



SCHEME 9.3 BDO synthesis from propylene oxide.



SCHEME 9.4 BDO production from butadiene.



SCHEME 9.5 BDO production from maleic anhydride.

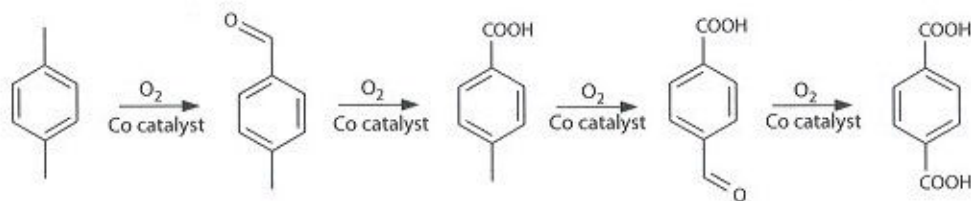
of BDO using a bio-based manufacturing process" [43]. Recently, Toray has successfully produced bio-based PBT from Genomatica's bio-based BDO. The bio-based PBT has equivalent physical properties to the petroleum-based PBT. DSM also announced their approval of bio-based BDO from the GENO BDO process in their Arnitel block-copolyester product line, where the hard segment is PBT.

BioAmber is another player in the bio-based BDO market. BioAmber started as a producer of bio-based succinic acid (SA) and later exclusively licensed DuPont's hydrogenation catalyst technology to produce bio-based BDO and tetrahydrofuran (THF) (from bio-based BDO). BioAmber has also built an exclusive partnership with Evonik to optimize DuPont's catalyst [44].

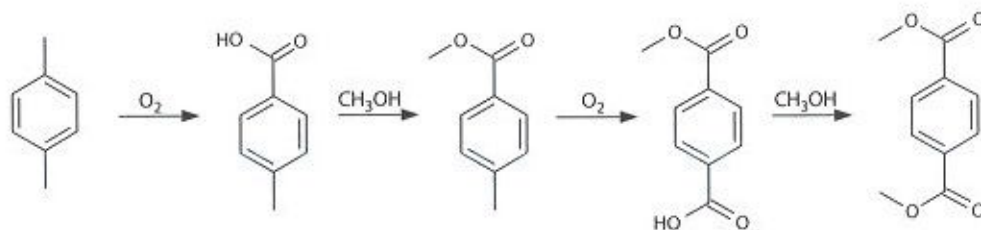
While progress has been made in the production of BDO from biorenewable resources, TPA and DMT production processes still rely on fossil-based feedstock. Both TPA and DMT manufacturing start with *p*-xylene as feedstock. The majority of TPA and DMT production worldwide is based on a cobalt/manganese/bromine catalyst developed by Scientific Design for oxidation of *p*-xylene [45]. In the process, acetic acid, which serves as the solvent, is charged into the reactor along with *p*-xylene and a catalyst. Excess compressed air is also charged into the reactor and reacts to oxidize the *p*-xylene. In this oxidation process, three intermediates are produced: *p*-tolualdehyde, *p*-toluic acid, and 4-formyl-benzoic acid, as shown in Scheme 9.6. The TPA produced precipitates from the acetic acid solvent due to its low solubility. During precipitation, a significant amount of 4-formyl-benzoic acid is trapped in the precipitate and prohibits further oxidation to TPA due to the similarity of TPA and 4-formyl-benzoic acid. TPA produced by this process contains such high amounts of residual 4-formyl-benzoic acid that it cannot be used to produce polyesters directly.

There are several processes to purify crude TPA and remove the residual 4-formyl-benzoic acid. One process was developed by Amoco Chemical [46] and accounts for the majority of the share of TPA feedstock for polyesters. The process is based on hydrogenation of 4-formyl-benzoic acid to *p*-toluic acid, followed by a series of crystallization steps of TPA [47]. The *p*-toluic acid is more soluble than TPA and remains in the liquid phase, while purified TPA crystals are precipitated out. Other processes include multistage oxidation, where after the oxidation process described previously, the slurry is transferred to another reactor and the temperature of the system is further increased. At the higher temperature, the TPA becomes more soluble in the slurry. The trapped 4-formyl-benzoic acid is then released and oxidized into TPA. Hydrolysis of DMT is another process used to produce a very small percentage of the TPA feedstock [48].

As in the production of TPA, the production of DMT also starts with *p*-xylene [48]. The *p*-xylene is first oxidized into *p*-toluic acid. Methanol is then added for the esterification reaction to form



SCHEME 9.6 Oxidation process to produce TPA.



SCHEME 9.7 DMT manufacturing process.

successfully produced
valent physical prop-
posed BDO from the
ard segment is PBT.
ed as a producer of
on catalyst technol-
(DO). BioAmber has
4].

resources, TPA and
MT manufacturing
dwide is based on a
of *p*-xylene [45]. In
along with *p*-xylene
acts to oxidize the
hyde, *p*-toluic acid,
ates from the acetic
of 4-formyl-benzoic
e similarity of TPA
amounts of residual

formyl-benzoic acid.
majority of the share
formyl-benzoic acid
-toluic acid is more
als are precipitated
cess described pre-
e system is further
slurry. The trapped
MT is another pro-

[48]. The *p*-xylene
on reaction to form

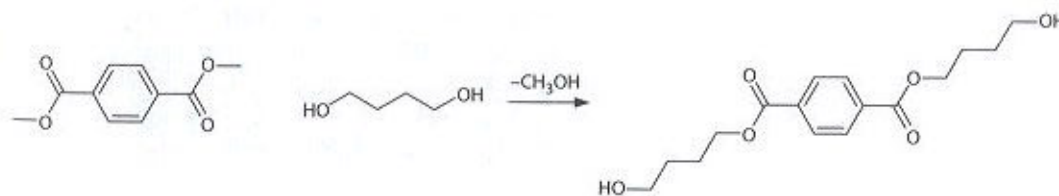
methyl *p*-toluate. In the following step, methyl *p*-toluate is oxidized to produce monomethyl terephthalate. Finally, methanol is again introduced to react with monomethyl terephthalate and produce DMT, as in Scheme 9.7. DMT can be purified easily by crystallization and distillation. In addition to this process, DMT can also be produced by direct esterification of crude TPA with methanol.

9.2.3 PBT POLYMERIZATION PROCESS

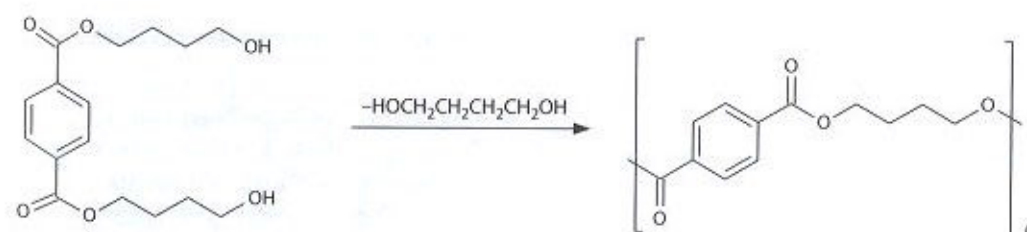
The synthesis chemistry of PBT has not changed significantly throughout the years, although there have been advances in processing and catalyst technology. Traditionally, the production of PBT resin started with DMT and BDO [49]. The first step is the transesterification reaction between DMT and BDO to produce the diester, bis(4-hydroxybutyl-terephthalate), or ester oligomers with hydroxybutyl ester end groups. Scheme 9.8 shows the diester structure. The reaction takes place at a temperature between 150°C and about 210°C, at atmospheric or slightly lowered pressure. During this first step, methanol is removed from the system as a by-product. The end of the first step is indicated by complete removal of methanol.

The second step is the polycondensation reaction of the diester or ester oligomers, during which the molecular weight of PBT is increased as the polycondensation reaction progresses (Scheme 9.9). The polycondensation takes place at temperatures close to 260°C and at a reduced pressure below 100 Pa [49]. In this step, BDO is constantly removed from the system as a by-product to advance the reaction. As the PBT molecular weight builds up, the melt viscosity increases significantly, which limits the rate of BDO removal. Hence, applied effective agitation is required to facilitate the BDO removal. The second step is completed when the desired molecular weight of PBT is achieved. The typical reaction time for the polycondensation step is 4 to 5 h. In industry, a common practice is to produce two grades of resin with high and low molecular weights. Any molecular weight between the two for a desired product or application can then be achieved by blending the low-molecular-weight and high-molecular-weight resins.

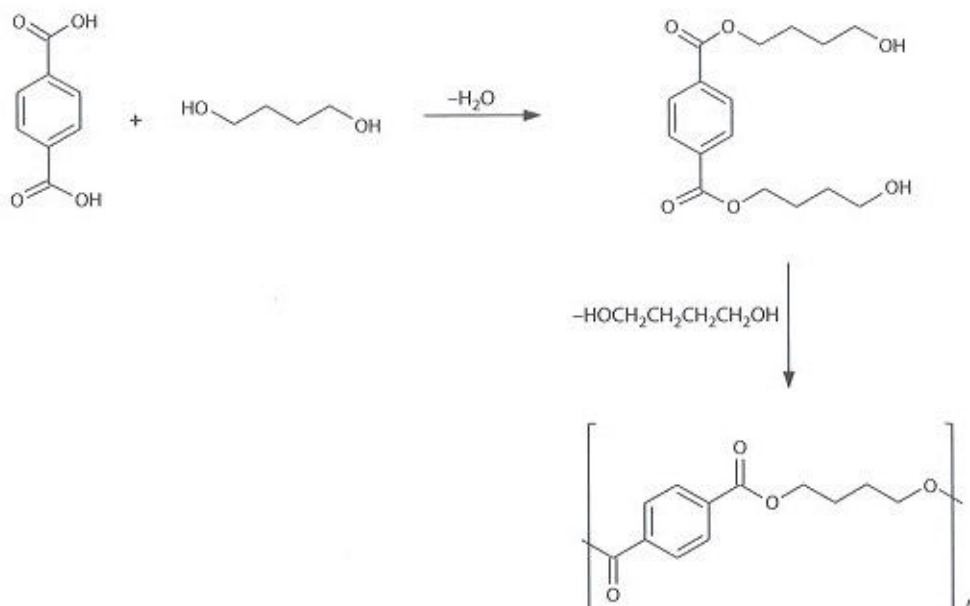
Due to the advancement of TPA purification technology and the lower price of TPA as a raw material, a new process using TPA and BDO as raw chemicals (shown in Scheme 9.10) has become less costly compared to the traditional process using DMT and BDO. Instead of transesterification between DMT and BDO to produce the diester or ester oligomers, the new process employs a direct



SCHEME 9.8 Transesterification of DMT and BDO.



SCHEME 9.9 Polycondensation step to produce PBT.

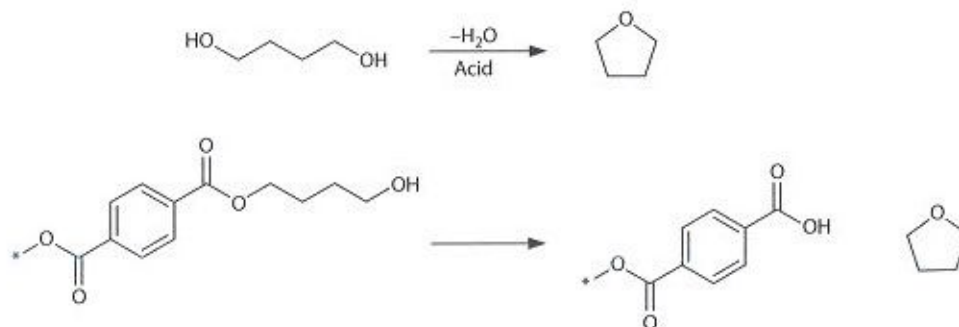


SCHEME 9.10 PBT from TPA and BDO.

esterification reaction of TPA with an excess amount of BDO [50–52]. During the reaction, water is removed from the reaction vessel. The second step of the process is to produce PBT from bis(4-hydroxybutyl-terephthalate). The ester oligomer formed is very similar for both routes, with either TPA or DMT as the starting raw material.

Industrial catalysts for PBT production are primarily titanium alkoxides, which can catalyze both direct esterification reactions and transesterification reactions [50,52]. In contrast to PET production, in PBT production, the same catalyst is used for both reactions due to its high efficiency. After PBT production, the catalyst remains in the resin and maintains its activity. Even at very low levels, these active catalysts can lead to other transesterification reactions when blended with other polymers such as PET and PC, but weak Lewis acids can be added into the blend to deactivate the catalysts [53,54].

The major side reaction in the production of PBT is the generation of THF [55–57]. The TPA-based process produces as much as twice the amount of THF by-product as that generated by the DMT-based process. Thus, another key point in making the TPA-based process more successful is to reduce THF formation during the reaction. THF forms in the reaction through two routes (Scheme 9.11) [58,59]. One is the acid-catalyzed dehydration of BDO, which is believed to cause



SCHEME 9.11 THF by-product formation.

the major amount of THF formation in the TPA-based process. The other route is backbiting of the hydroxybutyl ester end group to form BDO.

9.2.4 GREEN CHEMISTRY

Environmental awareness and the concept of sustainability have not only touched the raw materials aspect of PBT production, as previously mentioned for bio-based BDO, but have also promoted PBT production from postconsumer recycle (PCR) PET. PET is widely used as a packaging material for soft drinks, food, cosmetics, cooking oils, and many more products, and PET is the largest recycled plastic material in Europe. According to PETCORE Europe, in 2012, an equivalent of more than 60 billion PET bottles were recycled, which represents more than 52% of all postconsumer PET bottles [60].

One representative case of PBT production from PCR PET is IQ VALOX, produced by the Innovative Plastics business of SABIC. The process starts with PCR PET collection, sorting, cleaning, and grinding to produce PCR PET flakes. The PCR PET flakes are heated together with EG to break down the PET polymer chain and form bis-hydroxyethyl terephthalate (BHET) [61,62]. BDO is then added to make bis-hydroxybutyl terephthalate (BHBT) through a transesterification reaction. The next step is a polycondensation reaction to polymerize BHBT at elevated temperature and reduced pressure.

The process to make PBT from PCR PET is a chemical recycle process that degrades the PCR PET polymer chains to monomers or oligomers, and builds up the new PBT polymer chains from these monomers and oligomers. Unlike physical recycle processes by which the material performance will be deteriorated due to degradation and contamination, the PBT produced through a chemical recycle process from PCR PET is expected to have the same properties as PBT produced from virgin raw materials.

9.2.5 PBT CRYSTALLIZATION

PBT has very good chemical resistance, low moisture absorption, and relatively high strength and stiffness due to the existence of its crystalline phase. Typically, PBT has about 35% crystallinity [63]. The glass transition temperature of PBT is approximately 45°C [49] depending on the crystallinity, and the melting temperature is approximately 225°C [64]. The crystallinity, glass transition temperature, and melting temperature of PBT depend on the thermal history of the material. For instance, by annealing, the crystallinity of PBT can reach 60% [65–67]. Annealing of PBT for long periods of time can also shift the melting temperature and glass transition temperature toward higher values due to perfection of the ordered schemes. Various sizes of PBT crystals usually exist, and therefore, the differential scanning calorimetry (DSC) curve often shows multiple melting peaks. Understanding the thermal history of the PBT material is key to deciphering the DSC results.

PBT crystallizes in two different forms, the alpha form and the beta form, and both have a triclinic unit cell. For the alpha crystal, $a = 4.83 \text{ \AA}$, $b = 5.96 \text{ \AA}$, and $c = 11.62 \text{ \AA}$; $\alpha = 99.9^\circ$, $\beta = 115.2^\circ$, and $\gamma = 111.3^\circ$ [68,69]. For beta crystals, $a = 4.95 \text{ \AA}$, $b = 5.67 \text{ \AA}$, and $c = 12.95 \text{ \AA}$; $\alpha = 101.7^\circ$, $\beta = 121.8.2^\circ$, and $\gamma = 99.9^\circ$ [70]. The beta crystal usually forms under stress.

9.2.6 PBT PROPERTIES AND APPLICATIONS

PBT is an engineering thermoplastic that has applications in the automotive, electrical, electronics, health care, and building and construction markets, mainly for injection-molded parts. Although PBT can also be used to make fiber and film products, the applications of PBT in the form of fibers and films are far less than those for injection-molded parts. For fiber and film applications, PET plays the biggest role in the polyester family. PBT is limited in its capability to expand in this market due to its relatively high price along with its fast crystallization speed that results in a translucent rather than a transparent film.

In most injection-molding applications, PBT resin needs to be reinforced and enhanced with inorganic fillers to gain high modulus and strength. Among inorganic fillers, glass fiber is the most popular because it can achieve the desired properties at a relatively low cost. Other fillers for PBT include talc, clay, silica, mica, wollastonite, glass beads, and carbon fibers. Table 9.4 lists the properties of PBT and comparisons of PBT with glass fiber-filled PBT [71]. PBT resins are also formulated to various levels of flame resistance with flame-retardant and synergistic additives. Flame-retardant products are required for many applications such as electrical equipment, electronic devices, and home appliances. Typical flame-retardant ratings of PBT seen in the market are UL 94 V0 at 0.8, 1.6, and 3.2 mm, with slight differences in the vicinity of these thicknesses from different suppliers. A UL 94 5VA rating is also possible for PBT with a thickness of 2.0 mm or above [72].

Traditional flame retardants used for PBT are bromine-containing compounds or polymers [72], such as brominated carbonate oligomers, decabromodiphenyl ether (decaBDE), brominated PC, and brominated polystyrene. Antimony oxide can be added into the formulation for its synergistic effects with the primary flame-retardant additive.

However, with regulations on halogen-containing plastics becoming more stringent, it is often desirable to remove all halogen-containing flame-retardant agents from the PBT formulation for many applications. Some of the most successful alternatives are phosphorous-based flame retardants. The simplest phosphorous-based flame retardant for PBT is red phosphorous, which is also supplied in a coating form. The coating can help to reduce the toxic phosphine emitted during the processing [72].

A combination of nitrogen-based chemicals together with phosphorous-based flame retardants can also be used to flame-retard PBT. For example, PBT formulated with a combination of melamine pyrophosphate and resorcinol diphosphate can achieve a UL 94 rating of V0 at 0.8 mm [73].

In addition to PBT resin and reinforced PBT resin in various applications, PBT is also blended with other engineering thermoplastics to achieve unique combinations of properties. Blends of PBT with commercial significance include PBT/PET blends, PBT/PC blends, and impact-modified PBT.

PBT/PET blends are usually reinforced by glass fibers or minerals, similar to reinforced PBT [74]. Some physical and mechanical properties of glass fiber-reinforced PBT/PET blends are shown

TABLE 9.4
Typical Properties of PBT and Glass Fiber-Filled PBT Resins

Properties	Unit	Standard	PBT Resin	PBT+15% GF	PBT+20% GF	PBT+30% GF
Specific gravity	—	ASTM D792	1.31	1.40	1.44	1.53
Tensile strength	MPa	ASTM D638	55	90	115	125
Tensile elongation	%	ASTM D638	150	4	4	4
Flexural strength	MPa	ASTM D790	80	145	175	190
Flexural modulus	GPa	ASTM D790	2	5	6	8
Heat deflection temperature (1.82 MPa)	°C	ASTM D648	60	205	207	210
Izod impact strength (notched, room temperature)	kfg cm/cm	ASTM D256	5	5	7	10

Note: GF, glass fiber.

TABLE 9.5
Typical Properties of Glass Fiber-Reinforced PBT/PET Blends

Properties

Specific gravity
Tensile stress at break
Tensile strain at yield
Tensile modulus
Flexural modulus
Izod impact strength (notched, 23°C)
Instrumented impact total energy (23°C)
Heat deflection temperature (1.82 MPa, 3.2 mm, unannealed)

in Table 9.5. Although PBT and PET are both in the same phase, they crystallize separately. In glass fiber-reinforced PBT, glass fiber is the primary reinforcement. The mechanical properties of PBT/PET blends are similar to those of PET. In PBT/PET blends, the glass fiber should be undesirable if it happens to be hindered.

PBT/PC blends combine the high strength of PC and provides dimensional stability. PBT/PC blends provide good chemical resistance. However, PC causes transesterification reaction, a quenching reaction, a quenching reaction. The quencher is usually a quenching agent.

Impact-modified PBT blends with acrylate-butadiene-styrene (ABS) or butadiene-styrene (SEBS) to improve impact properties. In some cases,

9.3 POLYESTERS

The commercial success of PET has inspired further industrial development. One of the most important developments is the use of anedimethanol (CHDM) [81].

9.3.1 HISTORY OF CHDM

Linear polyesters synthesized from terephthalic acid and ethylene glycol are known as poly(1,4-cyclohexane dimethylene terephthalate) (PET) with a high melting point, and higher heat

TABLE 9.5
Typical Properties of Glass Fiber-Reinforced PBT/PET Blends

Properties	Unit	Standard	PBT/ PET+15% GF	PBT/ PET+30% GF	PBT/ PET+40% GF
Specific gravity	—	ASTM D792	1.43	1.54	1.64
Tensile stress at break	kgf/cm ²	ASTM D638	910	1070	1480
Tensile strain at yield	%	ASTM D638	3	3	2
Tensile modulus	kgf/cm ²	ASTM D638	50,900	81,500	130,000
Flexural modulus	kgf/cm ²	ASTM D790	45,800	71,300	108,900
Izod impact strength (notched, 23°C)	cm kgf/cm	ASTM D256	3	8	10
Instrumented impact total energy (23°C)	cm kgf	ASTM D3763	61	71	80
Heat deflection temperature (1.82 MPa, 3.2 mm, unannealed)	°C	ASTM D648	160	195	193

in Table 9.5. Although PBT and PET are miscible in the molten state as well as in the amorphous phase, they crystallize separately to form individual crystalline domains. Compared to glass fiber-reinforced PBT, glass fiber-reinforced PBT/PET blends have better surface appearance and gloss. The mechanical properties of the reinforced PBT/PET blends are dictated mainly by the glass fiber content. Another advantage of PBT/PET blends is their low cost due to the relatively low price of PET. In PBT/PET blends, transesterification may happen during processing [75], and this can be undesirable if it happens to the extent that crystallinity is reduced and fast crystallization is hindered.

PBT/PC blends combine the advantages of amorphous PC with crystalline PBT. Amorphous PC provides dimensional stability, good impact properties, and paint adhesion, while crystalline PBT provides good chemical resistance and heat performance. The remaining catalyst in the PBT resin causes transesterification to occur when PBT and PC are compounded [76]. To prohibit the transesterification reaction, a quencher is often added into the formulation to deactivate the catalyst [77]. The quencher is usually a phosphate salt such as zinc phosphate or mono zinc phosphate.

Impact-modified PBT blends are blends of PBT with impact modifiers [78–80], including methacrylate–butadiene–styrene (MBS), acrylonitrile–butadiene–styrene (ABS), and styrene–ethylene–butadiene–styrene (SEBS). The rubbery butadiene phase of the copolymers provides good impact properties. In some cases, these blends can maintain high impact properties at reduced temperatures.

9.3 POLYESTERS BASED ON CYCLOHEXANEDIMETHANOL

The commercial success of PET and PBT along with the quickly growing market of polyester fibers inspired further industrial research into new monomers for polyester synthesis during the 1950s. One of the most important and successful of these monomers was the high-heat diol 1,4-cyclohexanedimethanol (CHDM) developed by Tennessee Eastman Co., a division of Eastman Kodak Co. [81].

9.3.1 HISTORY OF CHDM-BASED POLYESTERS

Linear polyesters synthesized from cis- or trans-CHDM and TPA were patented in 1959 and became known as poly(1,4-cyclohexylenedimethylene terephthalate) (PCT) [82,83]. PCT is a crystalline polyester with a high melting point along with better weatherability, higher glass transition temperature, and higher heat distortion temperature than PET, and was reported be useful in forming

fibers and films [81]. PCT was first introduced by Tennessee Eastman as Kodel fiber, and a second line of Kodel fibers made from PET was later introduced by Eastman and then discontinued in the 1990s [84].

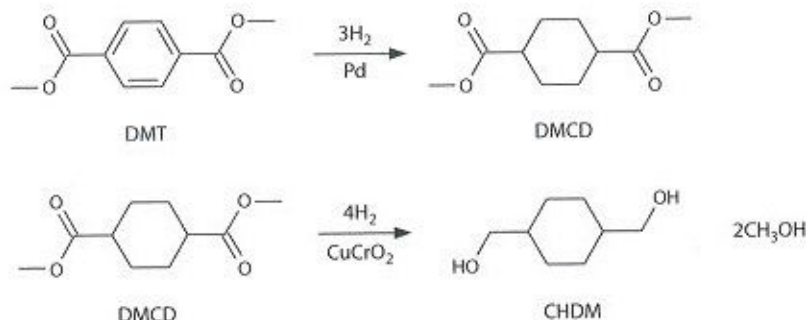
The original patents also disclosed the discovery of amorphous CHDM copolyesters, synthesized by polymerizing both EG and CHDM with TPA, but the first commercialization of an amorphous copolyester containing CHDM did not occur until many years later [81]. The amorphous poly(ethylene terephthalate-co-1,4-cyclohexylenedimethylene terephthalate) copolyesters are known as glycol-modified PCT (PETG) when the CHDM content is less than 50% and glycol-modified PCT (PCTG) when the CHDM content is greater than 50%. PETG was introduced by Eastman in 1977 as Kodar PETG 6763 and contained 70% EG and 30% CHDM [81]. The Eastman line of PETG and PCTG products has since been expanded to include several resins for injection-molding and blow-molding applications. Eastman later introduced PCT as an injection-molding resin in 1987 under the name Ektar, which included glass-reinforced PCT, but it is now called Thermx [85] and is owned by Celanese.

CHDM can also be polymerized with dimethyl trans-1,4-cyclohexanedicarboxylate (DMCD) or 1,4-cyclohexanedicarboxylic acid (CHDA) to yield completely aliphatic, cyclic, partially crystalline copolyesters known as poly(cyclohexylene dimethylene cyclohexanedicarboxylate) (PCCD). PCCD copolymers of trans-CHDA and CHDM that can form films and fibers were reported in 1959 [86]. However, they were not commercialized until many years later, most likely because of the exact stoichiometry needed to obtain high molecular weight and difficulty in crystallizing from the melt [87].

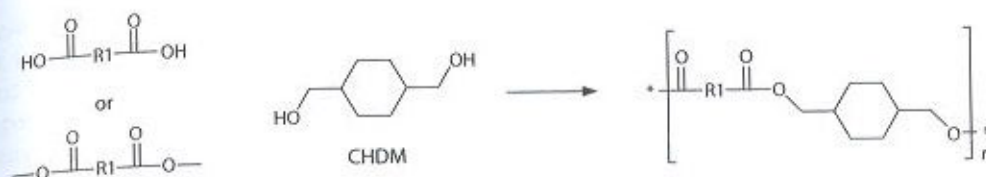
9.3.2 POLYMERIZATION PROCESS

The two major manufacturers of CHDM are currently Eastman Chemical in the United States and SK Chemical in Korea [88]. CHDM is a considerably more expensive diol monomer than EG but provides added value in properties such as higher heat and toughness compared to PET. The CHDM monomer is synthesized by catalytic hydrogenation of dimethylene terephthalate (DMT) in two steps, as shown in Scheme 9.12 [81]. DMT is first converted to dimethyl 1,4-cyclohexanedicarboxylate (DMCD), followed by conversion of DMCD to the CHDM diol [81]. The copper chromite catalyst is often used in industrial processes and yields a 70:30 trans/cis mixture of CHDM. The trans/cis ratio of the monomer isomers varies depending on the catalyst type and reaction conditions, and the ratio affects the properties of PCT and other polymers derived from CHDM [81].

Polyesters derived from CHDM are usually synthesized via a melt-phase polycondensation process with a metal catalyst in two steps, as shown in Scheme 9.13. Similar to other polyesters such as PET and PBT, the first step is an esterification with an excess of diols to form oligomers. This is followed by a second polycondensation step under high vacuum and elevated temperature to build



SCHEME 9.12 CHDM monomer synthesis by catalytic hydrogenation.



SCHEME 9.13 Polyester synthesis by polymerization of CHDM with diesters or diacids.

molecular weight [84]. The catalyst for the melt polymerization process can affect the molecular weight and color of the polymer formed. For PETG/PCTG synthesis, titanium catalysts are very active, but the copolymers tend to have a yellow color due to side reactions that also occur quickly [89]. Some catalysts such as antimony and cobalt yield polymers with a gray color due to reduction of the metals [90]. Combinations of manganese, zinc, titanium, and optional germanium catalysts with a phosphorus inhibitor and cobalt toning agent have been shown to reduce the yellow color of PETG/PCTG, and the material can be used in forming sheets [89,90]. Improvements in color and clarity have also been demonstrated by optimizing the process conditions to create a more active esterification product that requires lower catalyst amounts and reduced temperature for polycondensation, along with higher amounts of phosphorus stabilizer [91].

The main types of CHDM polyesters are shown in Table 9.6. PCT is the crystalline polyester generated from CHDM and DMT or TPA. PETG and PCTG are amorphous copolymers synthesized by the addition of EG in amounts above or below 50%, respectively, and acid-modified PCT (PCTA) is a crystalline copolyester synthesized by the addition of other diacids such as IPA at low levels. PCCD is produced from CHDM and DMCD to generate completely aliphatic copolymers. The thermal properties of each polyester are shown in Table 9.7, and mechanical properties are listed in Table 9.8.

TABLE 9.6
CHDM-Derived Polyesters and Copolymers

Diester/Diacid	Diol	Polymer
DMT/TPA	CHDM	PCT
TPA + IPA	CHDM	PCTA
DMT/TPA	CHDM (less than 50%) + EG	PETG
DMT/TPA	CHDM (greater than 50%) + EG	PCTG
DMCD	CHDM	PCCD

TABLE 9.7
Thermal Properties of CHDM-Derived Polyesters and Copolyesters

Polymer	T_g , °C	T_m , °C
PCT	60–95	250–290
	80–90	285–290
PCTA	88	230–280
PETG	81	—
PCTG	84	255
PCCD	40–70	205–235

TABLE 9.8
Mechanical Properties of CHDM-Derived Polyesters and Copolyesters

Polyester	PCT	PCTA	PETG	PCTG	PCCD
Specific gravity	1.2	1.2	1.27	1.23	1.13
Tensile stress at yield, MPa		47	50	45	13
Tensile stress at break, MPa	40–65	51	28	52	23
Elongation at yield, %	—	5	4.3	5	38
Elongation at break, %	170–350	300	110	330	400
Flexural modulus, MPa	1600–1900	1800	2100	1900	150
Izod impact strength, notched at 23°C, J/m	80–100	80	101	NB	—
Izod impact strength, notched at –40°C, J/m	—	40	37	64	40

Note: NB, no break.

9.3.3 PROPERTIES AND APPLICATIONS

CHDM polyesters generally have high strength, impact, transparency, and chemical resistance. CHDM is a unique monomer in that polymerization with the trans isomer yields PCT with a higher melting point of 315–320°C, while the cis isomer yields PCT with a melting point of 260–267°C [82]. Mixtures of isomers yield PCT polyesters with melting points of about 250–290°C [42]. The glass transition temperature of the polymer is also dependent on the trans/cis ratio of CHDM isomers. The T_g is about 60°C for PCT synthesized from cis-CHDM and 95°C for PCT from trans-CHDM. Methods have been developed to synthesize and isolate the higher-melting-point trans isomer [92], as well as to improve control over the trans/cis ratio [93]. Typical commercial PCT with a 70:30 trans/cis CHDM ratio crystallizes slower than PBT, at a rate similar to PET, although the crystallization rate is also dependent on the trans/cis ratio [84].

PCT was first used as a textile fiber [85]. Today, PCT is commonly used in connector applications, and the heat distortion temperature and stiffness can be enhanced further by the addition of glass filler. The heat deflection temperature (HDT) of 30% glass-filled PCT is typically 250–265°C, which is higher than that of glass-filled PET (220–230°C) or PBT (200–210°C) [94] but lower than liquid crystal polymers (288°C) [88].

Although its thermal properties are useful in many applications, the processing window of PCT is narrow due to its high melting point, which nearly approaches the decomposition temperature. To lower the melting point, PCT can be modified with low levels of other diacids, such as IPA to PCTA, a crystalline copolyester with good resistance to hydrolysis [85]. The IPA content in the copolyester is usually maintained at less than 25% to prevent difficulty in crystallization and the need to use artificial nucleation techniques [95]. PCTA is available as Durastar from Eastman Chemical, and

these copolyesters have a lower melting point and wider processing window than PCT but retain the transparency, toughness, and chemical and hydrolysis resistance [85]. PCTA has good hydrolytic stability and low moisture uptake due to its hydrophobic backbone and slower hydrolysis than copolyesters containing EG [81], and it requires less drying prior to processing. Most other CHDM-containing copolyesters must be dried carefully before processing to prevent loss of molecular weight and mechanical properties, although methods have been developed to reduce drying time and minimize hydrolytic degradation [96].

CHDM can also be incorporated into glycol-containing polyesters such as PET to produce amorphous polyesters, and the mole percent of CHDM in the copolyester influences the crystallization rate and melting temperature of the copolyester [81]. The mole percent of CHDM reduces the crystallinity and slows the crystallization rate of PET. An amorphous window where the polymers do not crystallize occurs around a ratio of about 70:30 EG/CHDM. As the level of CHDM is increased further, the melting point again becomes present and begins to increase along with the crystallization rate [96].

PETG copolyesters, as mentioned above, contain less than 50% CHDM and are useful in applications for containers and blow-molded bottles. They are often used in packaging and are produced as Spectar by Eastman Chemical Company [81]. PETG has been copolymerized with other monomers such as 2,6-naphthalene dicarboxylic acid (NDA) (0–40%) and SA (0–40%) to modify the T_g and shrinkage behavior [97]. At levels of CHDM greater than 50%, the copolyesters are known as PCTG. Due to the higher levels of CHDM, PCTG has higher impact strength, toughness, glass transition temperature, and heat distortion temperature but lower modulus than PETG. Both PETG and PCTG copolyesters have excellent transparency and are resistant to many organic solvents as well as γ -ray sterilization, rendering them useful in applications for kitchen and other household appliances or medical devices [81], along with automotive and electronic applications [98].

PCCD is a useful copolyester material for applications where greater ultraviolet (UV) stability and weatherability are required. Compared to PETG and PCTG, PCCD has better resistance to photooxidation as a result of its completely aliphatic nature. PCCD has a high melting point (225–235°C), but its lower crystallization temperature (152–171°C) and T_g (40–70°C) inhibit its usefulness in some applications [99]. The process conditions and stoichiometry have been optimized to enhance crystallinity [100], and various attempts have been made to increase the crystallinity and raise the T_g by incorporation of other aliphatic monomers such as bicyclo[2.2.2]octyl (DMCD-2) [101]. Amides such as 1,6-bis(4-carbomethoxycyclohexylcarboxamido) hexane have also been incorporated [99] and successfully raised T_g to 180–190°C without significantly affecting T_m . Incorporation of 2,2'-(sulfonylbis(4,1-phenyleneoxy))-bis(ethanol) is a method of raising the T_g of PCCD while maintaining low melt viscosity [102]. Higher amounts of trans-cyclohexyl diester isomer also raise the crystallization temperature, and attempts have been made to control reaction conditions by minimizing catalyst, temperature, and reaction time to maximize the trans/cis isomer ratio and lead to higher crystallization temperatures [87].

The widespread use of bisphenol A (BPA)-containing polymers and health concerns about BPA exposure has inspired development of several alternative, BPA-free copolyesters. In 2008, Eastman introduced Tritan, a copolyester derived from DMT, CHDM, and 2,2,4,4-tetramethyl-1,3-cyclobutanediol (TMCD) [103]. Its monomers and extracts have tested negative for estrogenic or androgenic activity [103]. Like PCTG/PETG and PCCD, Tritan is a tough, durable, transparent polyester with good impact and chemical resistance, and it is used for many similar applications such as bottles, housewares, small appliances, and medical devices [104].

ECOZEN is another BPA-free, bio-based copolyester of EG, TPA, CHDM, and isosorbide introduced by SK Chemicals in 2012 [105]. The isosorbide biomonomer is corn based and provides higher heat resistance than PETG [105]. ECOZEN has a heat distortion temperature of 80–110°C, with good chemical resistance and transparency, and has found applications in LED lighting, consumer electronics, housewares, and appliances [106].

PCCD

1.13
13
23
38
400
150
–
40

Unlike other polyesters such as PET and PBT, many CHDM-derived polyesters are miscible with PC over a wide compositional range and can be utilized to enhance the properties of PC blends. Blends of CHDM polyesters with PC are fully transparent and maintain good mechanical properties such as impact, tensile, and flexural strength, but with the added benefits of improved flow and hydrolysis resistance compared to traditional PC blends [107,108]. The polyesters also provide enhanced chemical resistance to a variety of solvents. Compared to PC alone, CHDM polyester/PC blends have improved resistance to ionizing radiation, demonstrating significantly reduced yellowing after exposure to various doses of gamma and electron beam radiation often used for sterilization of medical devices [109].

SABIC's Innovative Plastics business has developed the XYLEX product line based on transparent PC/amorphous polyester blends. In addition to clarity, XYLEX resins provide high impact strength; ductility; chemical resistance to solvents including cleaning fluids, automotive fluids, food and beverages, and alcohols; good weatherability; and high flow in selected grades [110]. XYLEX is useful in applications such as eyewear, health care, consumer electronics, housewares, and automotive [110,111].

9.4 NAPHTHALATE POLYESTERS

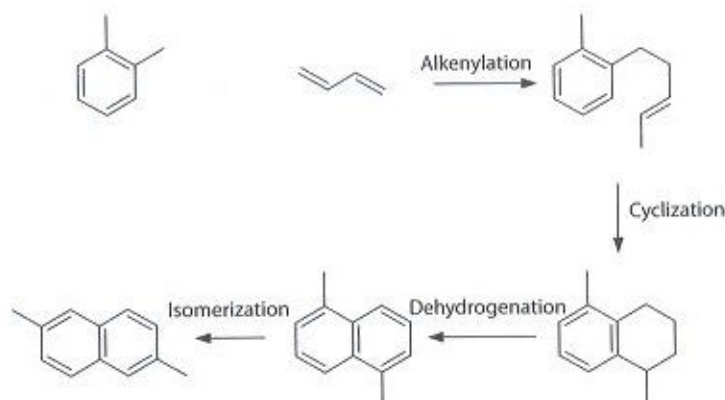
Concurrent with the invention of PET and PBT in the 1940s, other aromatic acid components were being explored as alternatives to TPA (or DMT). This resulted in the discovery and subsequent commercialization of naphthalate-based polyester poly(ethylene naphthalate) (PEN).

The aromatic monomer, namely, naphthalene dicarboxylic acid (NDA), is synthesized by the oxidation of 2,6-dialkyl naphthalene by cobalt/manganese or other catalysts with a promoter such as bromine [112]. Two minor impurities in the reaction include trimellitic acid and 2-formyl naphthoic acid (obtained from the partial oxidation of 2,6-dialkyl naphthalene) [112]. Additional products such as bromonaphthalene dicarboxylic acid are also observed in very small amounts [113]. In 1995, BP Amoco commercialized 2,6-naphthalene dicarboxylic acid dimethyl ester (NDC), produced from *o*-xylene and 1,4-butadiene, and NDC now sells up to 60 million lb./year. Other companies that followed Amoco in NDC production are Mitsubishi and Teijin of Japan. Even today, the high cost of NDC causes a niche market response to NDC-based polymers compared to commodity polymers like PET.

9.4.1 HISTORY

Prior to the piloting of PEN by Teijin in 1970, research was focused on an economical commercial route to manufacture NDC and NDA. The first attempts to make NDA (or NDC) mimicked the oxidation process of *p*-xylene to TPA. Instead of *p*-xylene, alkyl naphthalenes were oxidized to NDA [112]. Lillwitz [114] reviewed various other approaches for NDA production such as diiodonaphthalene, transcarboxylation, alkyl aromatic acylation, alkyl aromatic base-catalyzed condensations, and various aromatic alkylations.

The route chosen by BP Amoco for the production of NDA (or NDC) is the oxidation of 2,6-dimethyl naphthalene, derived from the alkenylation of *o*-xylene with 1,3-butadiene followed by subsequent cyclization, dehydrogenation, and isomerization (Scheme 9.14). Today, the cost of NDA remains expensive due to difficulties in the alkenylation of *o*-xylene with 1,3-butadiene. The stumbling block associated with alkenylation of *o*-xylene with 1,3-butadiene is primarily attributed to the very strong basic catalyst used in the reaction. Common bases, such as alkali metal oxides and alkali metal-exchanged zeolites, do not perform as well as the strongly basic sodium-potassium eutectic alloy (22 wt.% sodium and 78 wt.% potassium) [114]. It is paramount to invent novel a catalyst or process conditions that would drastically bring down the cost of NDA. Else, the market for NDA-based polymers will continue to be niche, in spite of being studied for over 60 years.



SCHEME 9.14 NDA process.

9.4.2 POLYMERIZATION PROCESS

Similar to other aromatic polyesters, the aromatic diacid (NDA or NDC) is polymerized with an aliphatic diol, mainly EG [115], propylene glycol, or butylene glycol, in the presence of a transesterification catalyst to produce PEN, poly(propylene naphthalate) (PTN) [116], or poly(butylene naphthalate) (PBN) [116], respectively. Compared to PEN, both PTN and PBN (commercialized by Teijin) are more expensive, and hence, most commercial interest generally involves studying PEN for various applications. Typical PEN polymerization processes are similar to those of PET and PBT, using excess diol to diacid (2:1 ratio) in the first stage to produce oligomers in the presence of a nitrogen atmosphere at a temperature range of 150–240°C, followed by further polymerization under vacuum at 290°C [115]. For PBN and PTN, the final polymerization temperature is lower, between 240°C and 255°C [116]. Due to the crystalline nature, SSP can also be used for polyesters such as PEN [117]. SSP not only reduces the color of the final polymer but also reduces degradation, which is important in developing useful applications involving both clarity and performance.

9.4.3 THERMAL PROPERTIES OF NAPHTHALATE POLYESTERS

Increasing the flexibility and length of the spacer from the shorter $-(CH_2)_2-$ in the case of EG used for PEN to the longer $-(CH_2)_4-$ in BDO used for PBN results in lowering of both T_g and T_m (Table 9.9) [118]. PBN has a significantly higher melting temperature compared to PTN, but PTN only has a moderate increase in glass transition temperature over PBN. Faster crystallization leads to a decrease in molding cycle time, which is very important for molding a greater number of parts in a shorter amount of time. PBT is currently the material of choice for faster molding cycles, but PBN can crystallize even faster than PBT. Compared to a crystallization time of 3 s for PBT, a mere 1 s is required for PBN.

TABLE 9.9
Thermal (T_g and T_m) Data of Naphthalate Polyesters

Property, °C	PEN	PTN	PBN
T_g	122	87	82
T_m	270	207	243

Source: Naphthalates. 2001. Engineering resin applications. BP. Available at <http://wenku.baidu.com/view/c560940f05087632311212dc.html>.

TABLE 9.10

Thermal Properties of Random Copolyesters Made from PPN and PTN:
 T_m (First Heating), ΔH_m (First Heating), and T_g (Second Heating)

Composition (Tere-Ester/Naph-Ester)	T_m , °C	ΔH_m , %	T_g , °C
100/0	227	77	47
92/8	221	70	50
85/15	212	62	52
70/30	192	52	57
65/35	185	48	59
55/45	169	37	65
45/55	150	35	67
35/65	169	29	71
25/75	176	34	75
10/90	199	42	82
0/100	207	47	87

Source: Lorenzetti, C., Finelli, L., Lotti, N., Vannini, M., Gazzano, M., Berti, C., and Munari, A.
Polymer, 46:4041, 2005.

In any crystalline polymer system, introducing defects by copolymerization will result in poor crystal lattice packing, and consequently, the melting point and percentage of crystallinity will decrease. Poly(1,3-propylene naphthalate) (PPN) was transesterified under melt with another polyester, namely, poly(1,3-propylene terephthalate) (PPT) [119], in the presence of a titanium tetrabutoxide catalyst at 260°C. The product was a random copolymer that displayed a reduction in both percentage of crystallinity as well as melting point, depending on the amount of comonomer in the system (Table 9.10). A gradual increase in T_g was also observed (Table 9.10).

Similarly, both PET/PEN random copolymers [120] as well as PET/PEN blends [120] had a lower melting point compared to the individual polymers due to entropy affecting the crystallization phenomena. At about 15% comonomer concentration (PET or PEN), the random copolymer essentially became amorphous [120], while the blends still showed a melting point [120]. Further, the blends showed higher T_m compared to copolymers of the same composition [120]. The difference in melting points of the same composition in a copolymer or blend is due to more homopolymer linkages in the case of the blend, leading to higher crystallinity and, hence, a higher melting point. Low- and high-naphthalate-content PET copolymers were commercialized by Shell company under the brand name HiPERTUF, targeted for packaging applications such as beer, food, carbonated drinks, hot fill, cosmetics, and pharmaceuticals.

Unlike melting temperature, the glass transition temperature of PEN/PET blends linearly increases with the ratio of PEN to PET [120], so that the T_g of new commercial products can easily be tailored by blending various amounts of PEN with PET. Practical applications include hot-filled, pasteurized, and washable containers, and outdoor glazing.

Similar to PET [121], PEN also exhibits a triclinic crystalline morphology (alpha and beta form) [122] (Table 9.11). Below 200°C, PEN crystallizes in the alpha form. At much higher temperatures, it crystallizes in the beta form.

9.4.4 GAS PERMEABILITY

PEN and PET are both slow-crystallizing polymers, meaning clear products such as films and bottles can be made. A major requirement for any bottle packaging is to provide a good barrier to gases,

TABLE 9.11
Crystal Unit Cell Data of PET and PEN

Polymer	a, nm	b, nm	c, nm	Alpha	Beta	Gamma
PET	0.49	0.594	1.075	98.5	118	112
PEN, alpha	0.651	0.575	1.32	81.33	144	100
PEN, beta	0.926	1.559	1.273	121.6	95.57	122.52

Source: Zhang, X. 2014. *Fundamentals of Fiber Science*. Lancaster, PA: DEStech; Ito, M. and Kikutani, T. 2002. PEN: Scheme and properties. In *Handbook of Thermoplastic Polymers: Homopolymers, Copolymers, Blends and Composites*, ed. S. Fakirov, 463–482. Weinheim: Wiley-VCH.

TABLE 9.12
Gas Transmission, cc mil/100 in.² day

Polymer	CO ₂ , Amorphous	CO ₂ , Oriented	O ₂ , Amorphous	O ₂ , Oriented	H ₂ O, Amorphous
PET	69	31	10.9	6.1	4.31
PEN	15	6	4.4	1.6	2.12

Source: Naphthalates. 2001. General properties of naphthalate-containing polymers. BP. Available at <http://wenku.baidu.com/view/0a24810bbb68a98271fefadf>.

and PEN showed significantly superior barrier performance compared to PET [120] (Table 9.12). The crystal orientation leads to closer packing of polymer chains, resulting in improved barrier performance over amorphous polymers. PTN is even more superior to PEN as a barrier for CO₂, and oxygen [118].

9.4.4.1 Gas Barrier Properties of PEN/PET Blends

Since PET is significantly cheaper than PEN, for all commercial practical purposes, adding more PET to blends with PEN significantly reduces the cost of the final product. Compared to the linear behavior for gas barrier properties of PET/PEN copolymers, actual data on the blends were significantly lower, indicating that the blends provided an improved barrier. This is attributed to the morphology of the PET and PEN domains, which directly influences the barrier [120].

9.4.5 CHEMICAL RESISTANCE

PEN is significantly superior to PET in terms of chemical, oxidative, and hydrolytic stability [120]. Improved chemical resistance is useful in applications such as packaging of pharmaceuticals, cosmetics, and chemicals (Table 9.13).

9.4.6 OPTICAL (UV) PROPERTIES

Unlike DMT, which does not absorb UV or visible light [120], NDC absorbs UV below 400 nm [120]. When polymerized, these monomers produce either PET or PEN, respectively. UV absorption occurs in PEN, while PET does not absorb UV light [120]. The UV absorption property causes PEN and other naphthalate polyesters/copolyesters to display improved UV barrier performance, resulting in greater retention of mechanical strength [120].

TABLE 9.13

Chemical Resistance Comparison between PET and PEN (Measured by Retention of Elongation at Break, %)

Polymer	10% HCl, 5 Weeks	10% NaOH, 2 Weeks	Ammonia Gas, 10 Weeks	Thermal Aging, 2 Weeks at 130°C, 100% Relative Humidity
PET	0	0	0	20
PEN	60	50	96	50

Source: Naphthalates. 2001. General properties of naphthalate-containing polymers. BP. Available at <http://wenku.baidu.com/view/0a24810bbb68a98271fefadf>.

9.4.7 FLUORESCENCE OF NAPHTHALATE POLYESTERS

Fluorescence is defined as the emission of light that was absorbed at a different wavelength. Due to the UV absorption property of naphthalate, polyesters containing naphthalate groups exhibit fluorescence [123]. PEN fluoresces a blue color when excited [123]. Among blends such as PET/PEN, the extent of fluorescence is directly related to the amount of naphthalate (PEN) present in the composition. With lower amounts of PEN, the blue color may not be visible. The fluorescence property can be used as an identification marker for naphthalate-containing compositions [123].

9.4.8 PHOTODEGRADATION

The formation of excited state dimers in naphthalate systems when exposed to sunlight or other sources such as UV results in the appearance of color (yellow) [124]. PEN is superior to PET during weathering, for this reason presence even a small amount of naphthalate improves the weathering performance of PET [118].

9.4.9 MECHANICAL PROPERTIES

Since PEN crystallizes slowly, Table 9.14 reflects the mechanical properties of amorphous PEN [118]. Compared to PET, generally superior performance in most of the properties is displayed by PEN [120]. Table 9.15 shows the mechanical properties against the ratio of PEN/PET for 50 μ m films and fibers [120]. PET shows better elongation compared to PEN. On the other hand, significant shrinkage is observed for PET, which could be due to the higher crystallization rate of PET over PEN.

9.4.10 NAPHTHALATE-BASED ELASTOMERS

It is well known that fast-crystallizing polymers such as PBT can be copolymerized with a flexible diol such as poly(ethylene glycol) to result in the formation of elastomers. Industrially, the most well-known elastomer is called Hytrel. Produced by DuPont, Hytrel is a copolymer of PBT having poly(tetramethylene oxide) flexible linkages. Since PBN crystallizes similarly to PBT, elastomers involving a poly(tetramethylene oxide) glycol soft linkage were also produced from PBN, and Table 9.16 lists the property comparison [118]. Higher melt temperatures combined with superior tensile strength and flex modulus were observed for PBN elastomers.

ntion

al Aging, 2 Weeks
°C, 100% Relative
Humidity

20
50

Available at <http://>

wavelength. Due
e groups exhibit
ds such as PET/
e (PEN) present
le. The fluores-
ng compositions

unlight or other
or to PET during
s the weathering

amorphous PEN
is displayed by
/PET for 50 µm
and, significant
ate of PET over

d with a flexible
trially, the most
er of PBT hav-
to PBT, elasto-
from PBN, and
ed with superior

TABLE 9.14**Mechanical Properties of Amorphous PEN**

Tensile strength yield, MPa	81.4
Elongation at yield, %	7.2
Ultimate tensile strength, MPa	47.6
Elongation at break, %	100
Flex modulus, MPa	2440
Tensile modulus, MPa	2400
Notch Izod, J/m	26.7
Tensile impact, J/m	0.25
Rockwell hardness, R scale	123

Source: Naphthalates. 2001. Engineering resin applications.
BP. Available at <http://wenku.baidu.com/view/c56094cf05087632311212dc.html>.

TABLE 9.15**Mechanical Property Comparison between PEN and PET**

Property	PEN/PET Ratio
Young's modulus, MD, MPa	1.31
Young's modulus, TD, MPa	1.27
Tensile strength, MD, MPa	1.39
Tensile strength, TD, MPa	1.36
Stress at 5% Elongation, MD, MPa	0.57
Stress at 5% Elongation, TD, MPa	0.7
Elongation at break, MD, %	0.57
Elongation at break TD, %	0.7
Thermal shrinkage at 150°C, MD %	0.46
Thermal shrinkage at 150°C, TD %	0.30
Fiber tenacity, g/den	1.1
Fiber modulus, g/den	3.27
Fiber elongation at break, %	0.57
Fiber boiling water shrinkage, %	0.2
Fiber dry heat shrinkage at 177°C, %	0.5

Source: Naphthalates. 2001. General properties of naphthalate-containing polymers. BP. Available at <http://wenku.baidu.com/view/0a24810bbb68a98271fefadf>.

Note: MD, machine direction; TD, transverse direction.

9.4.11 APPLICATIONS

The main applications of naphthalate polyesters are in the area of films, fibers, and containers. Films, such as the Teonex brand of PEN films produced by Teijin, are sold for high-density data storage tapes, integrated circuit cards, automotives, capacitors, electrical insulation, batteries, and opticals. Fibers, such as Performance Fibers A-701, are sold for tire and industrial applications. Container applications include food, beer, carbonated drinks, hot-fill juices, cosmetics, and pharmaceuticals, using materials such as Shell's HiPERTUF PET/PEN copolymer.

TABLE 9.16
Elastomer Comparison Having Hard Blocks of PBT or PBN

Property	PBN Elastomer	PBT Elastomer
Specific gravity,	1.21	1.12
Shore D hardness,	55	47
Melt temperature, °C	225	182
Vicat temperature, °C	190	127
Tensile strength at yield, MPa	16.4	7.8
Elongation at yield, %	20	50
Tensile strength at break, MPa	26.3	18.8
Tensile elasticity, MPa	34.8	45.1
Flex modulus, MPa	139.4	70.6
Taber abrasion, mg/1000	16	12
Volume resistivity, omega, cm	1.50×10^{15}	1.80×10^{12}

Source: Naphthalates. 2001. Engineering resin applications. BP. Available at <http://wenku.baidu.com/view/c56094cf05087632311212dc.html>.

REFERENCES

1. Carraher, Jr., C.E. 2014. *Polymer Chemistry*. Boca Raton, FL: Taylor & Francis.
2. Whinfield, J.R. 1946. Chemistry of terylene. *Nature*, 158:930-931.
3. Billica, H.R. 1951. Production of polyethylene terephthalate using antimony trioxide as polymerization catalyst. US Patent 2647885A.
4. Thomas, R.R. 1966. Preparation of antimony triacetate. US Patent 3415860A.
5. Julliard, G.C., Therese, J.M., Perry, M., Wayne, W.A., and Cheuk, Y. 1999. Preparation of polyesters employing antimony catalysts and acidic phosphorus compounds. WO Patent 2001014452A1.
6. Jen, Z.C. 2001. Manufacturing method for decreasing the cyclic oligomer content in polyester. US Patent 6392005B1.
7. Finley, M.E., Nicholas, R.C., and Ronald, T.A. 1974. Process and catalyst-inhibitor system for preparing synthetic linear polyester. US Patent 3907754A.
8. Bashir, Z., Munif, A.M., Rao, M.V., and Padmanabhan, S. 2010. Process for making polyethylene terephthalate. WO Patent 2011020619A1.
9. Cholod, M.S. and Shah, N.M. 1982. Catalyst system for a polyethylene terephthalate polycondensation. US Patent 4356299A.
10. Bander, J.A., Lazarus, S.D., and Twilley, I.C. 1980. Catalytic process for preparation of polyesters. US Patent 4260735A.
11. John, P.A. and Mary, J.S. 1967. Preparation of polyethylene terephthalate using cyanide esterification catalyst. US Patent 3451973A.
12. Charles, Jr., H.H. 1951. Production of polyethylene terephthalate with cobaltous acetate as catalyst. US Patent 2641592A.
13. Patrick, H.H. 1955. Stannous formate catalyst for preparing polyethylene terephthalate. US Patent 2892815A.
14. James, B.B., William, K.E., and Julian, K.L. 1955. Catalytic production of polyethylene terephthalate. US Patent 2857363A.
15. Joseph, G.N. and John, J.V. 1969. Stibinic and stibonic catalysts for polyethylene terephthalate. US Patent 3642702A.
16. Siggel, E., Koepp, H.M., and Rein, W. 1966. Process for the production of polyethylene terephthalate. US Patent 3398124A.
17. Emmette, F.I. 1948. Production of polyethylene terephthalate. US Patent 2534028A.
18. John, A.P. and Mary, J.S. 1967. Process of preparing polyethylene terephthalate using lead fluoride as transesterification catalyst and as condensation catalyst. US Patent 3457239A.

19. Hartmann, A., Forster, P.F., and Otto, V.O.H. 1965. Process for manufacturing polyethylene terephthalate employing metal salts of halogenated aliphatic acids. US Patent 3385830A.
20. Nyce, G.W., Lamboy, J.A., Connor, E.F., Waymouth, R.M., and Hedrick, J.L. 2002. Expanding the Catalytic Activity of Nucleophilic N-Heterocyclic Carbenes for Transesterification Reactions. *Org. Lett.*, 4(21):3587-3590.
21. Bartolome, L., Imran, M., Cho, B.G., Al-Masry, W.A., and Kim, D.H. 2012. Recent developments in the chemical recycling of PET. In *Material Recycling—Trends and Perspectives*, ed. Achilias, D. Available at <http://www.intechopen.com/books/material-recycling-trends-and-perspectives/recent-developments-in-the-chemical-recycling-of-pet>.
22. Papaspyrides, C.D. and Vouyouka, S.M. 2009. *Solid State Polymerization*. Hoboken, NJ: John Wiley & Sons.
23. Duh, B. 2006. Effects of crystallinity on solid-state polymerization of poly(ethylene terephthalate). *J. Appl. Polym. Sci.*, 102(1):623-632.
24. Fakirov, S. 1997. Polyethylene terephthalate. In *Handbook of Thermoplastics*, ed. Olabisi, O., 449-464. New York: Marcel Dekker.
25. Scheirs, J. 2000. *Compositional and Failure Analysis of Polymers: A Practical Approach*. New York: John Wiley & Sons.
26. Dixon, E.R. and Jackson, J.B. 1968. The inter-relation of some mechanical properties with molecular weight and crystallinity in poly(ethylene terephthalate). *J. Mater. Sci.*, 3:464.
27. Tewarson, A. 2003. Flammability of polymers. In *Plastics and the Environment*, ed. Andrady, A.L., 403-489. Hoboken, NJ: John Wiley & Sons.
28. Schiers, J. 2003. Additives for the modification of poly(ethylene terephthalate) to produce engineering-grade polymer. In *Modern Polyesters*, eds. Schiers, J. and Long, T.E., 495-540. Chichester: John Wiley & Sons.
29. Largman, T. 1981. Phosphine suppressants for polymeric compositions including red phosphorus as a flame retardant. US Patent 4356282A.
30. Schlechter, M. 2013. *Engineering Resins, Polymer Alloys and Blends: Global Markets*. BCC Research, Wellesley, MA.
31. Gallucci, R. and Patel, B. 2003. Poly(butylene terephthalate). In *Modern Polyesters: Chemistry and Technology of Polyesters and Copolyesters*, eds. Scheirs, J. and Long, T.E. Chichester: John Wiley & Sons.
32. Available at <http://www.celanese.com/engineered-materials/products/Celanex--PBT/What-is-PBT.aspx>.
33. Copenhaver, J.W. and Bigelow, M.H. 1949. *Acetylene and Carbon Monoxide Chemistry*. New York: Reinhold.
34. Haas, T., Jaeger, B., Weber, R., Mitchell, S.F., and King, C.F. 2005. New diol processes: 1,3-propanediol and 1,4-butanediol. *Appl. Catal. A: Gen.*, 280(1):83-88.
35. Dehler, J., Hoffmann, H., Joschek, H.I., Reiss, W., Schnur, R., and Winderl, S. 1978. Manufacture of butynediol. U.S. Patent No. 4,093,668. Washington, DC: U.S. Patent and Trademark Office.
36. Hoffmann, H., Reiss, W., Schroeder, W., and Winderl, S. 1978. Manufacture of butynediol. U.S. Patent No. 4,067,914. Washington, DC: U.S. Patent and Trademark Office.
37. Hoffmann, H., Reiss, W., Schnur, R., Winderl, S., and Zehner, P. 1976. Process for the manufacture of butynediol. U.S. Patent No. 3,957,888. Washington, DC: U.S. Patent and Trademark Office.
38. Sampat, B.J. 2011. 1,4-Butanediol: A techno-commercial profile. *Chemical Weekly*. Available at <http://www.chemicalweekly.com/Profiles/1,4-Butanediol.pdf>.
39. Mueller, H. 1995. Tetrahydrofuran. In *Ullmann's Encyclopedia of Industrial Chemistry*. Weinheim: Wiley-VCH.
40. Kouba, J.K. and Snyder, R.B. 1987. Coproduction of butanediol and tetrahydrofuran and their subsequent separation from the reaction product mixture. U.S. Patent No. 4,656,297. Washington, DC: U.S. Patent and Trademark Office.
41. Felthouse, T.R. 1998. Growing maleic anhydride through its uses and processes. *Chemist*, 75(5):22-27.
42. Burk, M.J., Van Dien, S.J., Burgard, A.P., and Niu, W. Compositions and methods for the biosynthesis of 1,4-butanediol and its precursors. US Patent US8067214 B2.
43. Available at <http://www.genomatica.com/news/press-releases/successful-commercial-production-of-5-million-pounds-of-bdo/>.
44. Available at http://www.bio-amber.com/products/en/products/bdo_1_4_butanediol.
45. Saffer, A. and Barker, R.S. 1958. Preparation of aromatic polycarboxylic acids. US Patent 2833816 A.
46. Meyer, D. 1967. Fiber-grade terephthalic acid by catalytic hydrogen treatment of dissolved impure terephthalic acid. US Patent 3584039.

47. Fisher, J. 1973. Terephthalic acid recovery by continuous flash crystallization. US Patent 3931305.
48. Sheehan, R. 1995. Terephthalic acid, dimethyl terephthalate, and isophthalic acid. In *Ullmann's Encyclopedia of Industrial Chemistry*. Weinheim: Wiley-VCH.
49. Antic, V.V. and Pergal, M.V. 2011. Poly(butylene terephthalate)—Synthesis, properties, applications. In *Handbook of Engineering and Specialty Thermoplastics*, eds. Thomas, S. and Visakh, P.M. Beverly, MA: Scrivener Publishing.
50. Hoeschele, G.K. and McGrik, R.H. 1992. Process for preparing polyesters using a catalyst mixture of tetraalkyl titanates and zirconates. EP0472179 A2.
51. Kawaguchi, K., Nakane, T., and Hijikata, K. 1994. Process for the preparation of polyester resin. EP0578464 A1.
52. Griebler, W.-D., Hirschberg, E., Hirthe, B., Schmidt, W., and Thiele, U. 2003. Titanium containing catalyst and process for production of polyester. EP0736560 B1.
53. Lei, C. and Chen, D. 2008. Effect of di-n-dodecyl phosphate on the transesterification reaction in a poly(butylene terephthalate)/polycarbonate blend. *J. Appl. Polym. Sci.*, 109(2):1099–1104.
54. Van Bennekom, A.C.M., Van Den Berg, D., Bussink, J., and Gaymans, R.J. 1997. Blends of amide modified polybutylene terephthalate and polycarbonate: Phase separation and morphology. *Polymer*, 38(20):5041–5049.
55. Komatsu, Y., Matano, K., and Suzuki, S. 1998. Manufacture of white poly(butylene terephthalate) with low amount of THF generation. JP10243740.
56. Ramaraju, D., Ravi, G.R., Starkey, K., Donovan, M., and Agarwal, P. 2007. Process of making polyesters. US20070197738 A1.
57. Chang, S.J. and Tsai, H.B. 1992. Effect of salts on the formation of THF in preparation of PBT by TPA process. *J. Appl. Polym. Sci.*, 45(2):371–373.
58. Pilati, F., Manaresi, P., Fortunato, B., Munari, A., and Passalacqua, V. 1981. Formation of poly(butylene terephthalate): Growing reactions studied by model molecules. *Polymer*, 22(6):799–803.
59. Pilati, F., Manaresi, P., Fortunato, B., Munari, A., and Passalacqua, V. 1981. Formation of poly(butylene terephthalate): Secondary reactions studied by model molecules. *Polymer*, 22(11):1566–1570.
60. Petcore Europe press release. 2014. More than 60 billion PET bottles recycled 2012! Available at <http://www.petcore.org/news/more-60-billion-pet-bottles-recycled-2012>.
61. Agarwal, P., Cohoon, K., and Dhawan, S. et al. 2010. Use scrap PET to make PBT thermoplastic molding compositions involves depolymerizing PET in presence of alcohol; butanediol used to make polybutylene terephthalate can come from biomass (i.e. renewable monomer); energy savings/reduced carbon dioxide emissions by use of waste PET. US Patent 7799836 B2.
62. Agarwal, P., Cohoon, K., and Dhawan, S. et al. 2012. Process for making polybutylene terephthalate (PBT) from polyethylene terephthalate (PET). US Patent 8088834 B2.
63. Cheng, S.Z.D., Pan, R., and Wunderlich, B. 1988. Thermal analysis of poly(butylene terephthalate) for heat capacity, rigid-amorphous content, and transition behavior. *Macromol. Chem.*, 189(10):2443–2458.
64. Smith, J.G., Kibler, C.J., and Sublett, B.J. 1966. Preparation and properties of poly(methylene terephthalate). *J. Polym. Sci., Part A*, 4(7):1851–1859.
65. Jaquiss, D.B.G., Borman, W.F.H., and Campbel, R.W. 1982. Polyesters, thermoplastics. In *Encyclopedia of Chemical Technology*, eds. Mark, H.F., Othmer, D.F., Overberger, C.G., and Seaborg, G.T., 549–574. New York: John Wiley & Sons.
66. Chang, E.P., Kirsten, R.O., and Slagowski, E.L. 1978. The effect of additives on the crystallization of poly(butylene terephthalate). *Polym. Eng. Sci.*, 18(12):932–936.
67. Illers, K.H. 1980. Heat of fusion and specific volume of poly(ethylene terephthalate) and poly(butylene terephthalate). *Colloid. Polym. Sci.*, 258(2):117–124.
68. Mencick, Z. 1975. The crystal structure of poly(tetramethylene terephthalate). *J. Polym. Sci.: Polym. Phys. Ed.*, 13(11):2173–2181.
69. Stambaugh, B., Koenig, J.L., and Lando, J.B. 1979. X-ray investigation of the structure of poly(tetramethylene terephthalate). *J. Polym. Sci.: Polym. Phys. Ed.*, 17(6):1053–1062.
70. Yokouchi, M., Sakakibara, Y., Chatani, Y., Tadokoro, T., Tanaka, T., and Yoda, K. 1976. Structures of two crystalline forms of poly(butylene terephthalate) and reversible transition between them by mechanical deformation. *Macromolecules*, 9(2):266–273.
71. CCP PBT datasheet. Available at <http://www.ccp.com.tw/>.
72. Weil, E.D. and Levchik, S.V. 2004. Commercial flame retardancy of thermoplastic polyesters—A review. *J. Fire Sci.*, 22(4):229–350.
73. Penn, R. 1998. Flame retarded poly(butylene terephthalate) composition. US Patent 5,814,690.

74. Vu-Khanh, T., Denault, J., Habib, P., and Low, A. 1991. The effect of injection molding on the mechanical behavior of long-fiber reinforced PBT/PET blends. *Compos. Sci. Technol.*, 40(4):423-435.
75. Montaudo, G., Puglisi, C., and Samperi, F. 1998. Mechanism of exchange in PBT/PC and PET/PC blends. Composition of the copolymer formed in the melt mixing process. *Macromolecules*, 31(3):650-661.
76. Porter, R.S. and Wang, L.H. 1992. Compatibility and transesterification in binary polymer blends. *Polymer*, 33(10):2019-2030.
77. Clark, A.H., Courson, R.D., Gallucci, R.R., and Walsh, E.B. 1995. High density polyester-polycarbonate molding composition. US Patent 5,441,997.
78. Wu, J., Mai, Y.W., and Cotterell, B. 1993. Fracture toughness and fracture mechanisms of PBT/PC/IM blend. *J. Mater. Sci.*, 28(12):3373-3384.
79. Wang, X.H., Zhang, H.X., Wang, Z.G., and Jiang, B.Z. 1997. Toughening of poly(butylene terephthalate) with epoxidized ethylene propylene diene rubber. *Polymer*, 38(7):1569-1572.
80. Mohd Ishak, Z.A., Ishiaku, U.S., and Karger-Kocsis, J. 1999. Hygrothermal aging and fracture behavior of styrene-acrylonitrile/acrylate based core-shell rubber toughened poly(butylene terephthalate). *J. Appl. Polym. Sci.*, 74(10):2470-2481.
81. Turner, S.R. 2004. Development of amorphous copolyesters based on 1,4-cyclohexane-dimethanol. *J. Polym. Sci., Part A: Polym. Chem.*, 42(23):5847-5852.
82. Kibler, C.J., Bell, A., and Smith, J.G. 1959. Linear polyesters and polyester-amides from 1,4-cyclohexanedimethanol. US Patent 2,901,466.
83. Kibler, C.J., Bell, A., and Smith, J.G. 1962. Linear polyester of 1,4-cyclohexanedimethanol and amino-carboxylic acids. US Patent 3,033,826.
84. East, A.J. 2006. Polyesters, thermoplastic. In *Kirk-Othmer Encyclopedia of Chemical Technology*, eds. A. Seidel and M. Bickford. 31-95. New York: John Wiley & Sons.
85. Turner, S.R., Seymour, R.W., and Dombroski, J.R. 2004. Amorphous and crystalline polyesters based on 1,4-cyclohexanedimethanol. In *Modern Polyesters: Chemistry and Technology of Polyesters and Copolyesters*, eds. Scheirs, J. and Long, T.E. Chichester: John Wiley & Sons.
86. Caldwell, J.R. and Gilkey, R. 1959. Fiber-forming polyesters from trans-1,4-cyclohexanedicarboxylic compounds and 1,1-cyclohexane dimethanol. US Patent 2,891,930.
87. Brunelle, D.J. and Jang, T. 2006. Optimization of poly(1,4-cyclohexylidene cyclohexane-1,4-dicarboxylate) (PCCD) preparation for increased crystallinity. *Polymer*, 47(11):4094-4104.
88. Leaversuch, R.D. 2004. Thermoplastic polyesters: It's a good time to know them better. *Plastics Technology*. Available at <http://www.ptonline.com/articles/thermoplastic-polyesters-it's-a-good-time-to-know-them-better>.
89. Yau, C.C. and Cherry, C. 1995. Copolyester of cyclohexanedimethanol and process for producing such polyester. US Patent 5,385,773.
90. Yau, C.C. and Cherry, C. 1994. Copolyester of cyclohexanedimethanol and process for producing such polyester. US Patent 5,340,907.
91. Adams, V.S., Hataway, J.E., and Roberts, K.A. 1997. Process for preparing copolyesters of terephthalic acid ethylene glycol and 1,4-cyclohexanedimethanol exhibiting a neutral hue high clarity and increased brightness. US Patent 5,681,918.
92. Hasek, R.H. and Knowles, M.B. 1959. Preparation of trans-1,4-cyclohexanedimethanol. US Patent 2,917,549.
93. Rathmell, C., Spratt, R.C., and Tuck, M.W.M. 1995. Preparation of cyclohexanedimethanol with a particular ratio. US Patent 5,395,987.
94. Sastri, V.R. 2010. Engineering thermoplastics: Acrylics, polycarbonates, polyurethanes, polyacetals, polyesters, and polyamides. In *Plastics in Medical Devices: Properties, Requirements, and Applications*, 121-173. Amsterdam: Elsevier.
95. Schulken, R.M., Boy, R.E., and Cox, R.H. 1964. Differential thermal analysis of linear polyesters. *J. Polym. Sci., Part C*, 6(1):17-25.
96. Dickerson, J.P., Brink, A.E., Oshinski, A.J., and Seo, K.S. 1997. Copolyesters based on 1,4-cyclohexanedimethanol having improved stability. US Patent 5,656,715.
97. Tsai, Y., Fan, C.H., Hung, C.Y., and Tsai, F.J. 2008. Amorphous copolyesters based on 1,3/1,4-cyclohexanedimethanol: Synthesis, characterization and properties. *J. Appl. Polym. Sci.*, 109(4):2598-2604.
98. Turner, S.R., Seymour, R.W., and Smith, T.W. 2001. Cyclohexanedimethanol polyesters. In *Encyclopedia of Polymer Science and Technology*. Hoboken, NJ: John Wiley & Sons.
99. Brunelle, D.J. 1999. Polyesteramides of high crystallinity and reagents for their preparation. US Patent 5,939,519.

100. Patel, B.R., Smith, G.F., and Banach, T.E. 1999. Crystalline polyester resins and process for their preparation. US Patent 5,986,040.
101. Liu, Y. and Turner, S.R. 2010. Synthesis and properties of cyclic diester based aliphatic copolyesters. *J. Polym. Sci., Part A: Polym. Chem.*, 48(10):2162–2169.
102. Turner, S.R. and Sublett, B.J. 2000. Low melt viscosity amorphous copolyesters with enhanced glass transition temperatures. US Patent 6,120,889.
103. Kline, T.R. and Ruhter, M.C. 2012. Alternatives analysis report for bisphenol-A in infant formula cans and baby food jar lids. Published by Maine Department of Environmental Protection. Available at <http://www.maine.gov/dcp/safechem/documents/AAR-Report-December2012.pdf> (accessed July 21, 2015).
104. Available at http://www.eastman.com/Brands/Eastman_Tritan/Pages/Overview.aspx.
105. Laird, K. 2012. Green matter: A dash of isosorbide makes all the difference. *Plastics Today*. Available at <http://www.plasticstoday.com/blogs/green-matter-dash-isosorbide-makes-all-difference-112920121>.
106. Available at http://www.skchemicals.com/korean/product/ecozen/sub/sub_overview.asp?menu=11.
107. Scott, S.W. 1983. Thermoplastic molding composition. US Patent 4,391,954.
108. Scott, S.W. 1995. Thermoplastic molding composition. US Patent 5,478,896.
109. Allen, R.B. and Avakian, R.W. 1988. Method for enhancing ionizing radiation. US Patent 4,778,656.
110. Innovative Plastics: RESISTANCE+DURABILITY: Chemical Resistance Performance Testing for Healthcare Materials. Available at http://www.pod-sabic-ip.com/KBAM/Reflection/Assets/Thumbnail/22863_3.pdf (accessed July 21, 2015).
111. VERSATILITY + DURABILITY: XYLEX™ PC/POLYESTER RESIN. Available at http://www.pod-sabic-ip.com/KBAM/Reflection/Assets/Thumbnail/7129_15.pdf (accessed October 12, 2014).
112. Yamashita, G. and Yamamoto, K. 1972. Process for the preparation of 2,6-naphthalenedicarboxylic acid. US Patent 3870754.
113. McMahon, R.F., Greene, Jr., J.D., and Peterson, D.A. 1997. Process for preparing 2,6-naphthalenedicarboxylic acid. US Patent 6114575.
114. Lillwitz, L.D. 2001. Production of dimethyl-2,6-naphthalenedicarboxylate: Precursor to polyethylene naphthalate. *Appl. Catal. A*, 221:337.
115. Lee, K.K., Cho, B.H., and Kim, Y.W. 1993. Process for preparing polyethylene naphthalate. US Patent 5294695.
116. Kulkarni, S. and Raj, B. 2007. Naphthalate based polyester resin compositions. US Patent 20070232763 A1.
117. Kwon, I.-H., Bang, Y.-H., Lee, J., Lee, D.-J., and Lee, I.-H. 2003. High tenacity polyethylene-2,6-naphthalate fibers. European Patent 1510604 B1.
118. Naphthalates. 2001. Engineering resin applications. BP. Available at <http://wenku.baidu.com/view/c56094cf05087632311212dc.html>.
119. Lorenzetti, C., Finelli, L., Lotti, N., Vannini, M., Gazzano, M., Berti, C., and Munari, A. 2005. Synthesis and characterization of poly(propylene terephthalate/2,6-naphthalate) random copolyesters. *Polymer*, 46:4041.
120. Naphthalates. 2001. General properties of naphthalate-containing polymers. BP. Available at <http://wenku.baidu.com/view/0a24810bbb68a98271fefadf>.
121. Zhang, X. 2014. *Fundamentals of Fiber Science*. Lancaster, PA: DEStech.
122. Ito, M. and Kikutani, T. 2002. PEN: Scheme and properties. In *Handbook of Thermoplastic Polymers: Homopolymers, Copolymers, Blends and Composites*, ed. S. Fakirov, 463–482. Weinheim: Wiley-VCH.
123. Santhanagopalakrishnan, P. and Kulkarni, S.T. 2008. Polyester resins. In *Polyesters and Polyamides*, eds. Deopura, B.L., Alagirusamy, R., Joshi, M., and Gupta, B., 1–40. Boca Raton, FL: CRC Press.
124. Marien, A., Hagemann, J., and Weber, B. 1998. Polyalkylene naphthalene film comprising specific UV-absorber. US patent 5824465.

Materials Science and Engineering

SECOND EDITION HANDBOOK OF THERMOPLASTICS



"The second edition of the *Handbook of Thermoplastics* offers an important update since the first edition. New subjects have been added for areas emerging of interest since the first edition. Having utilized the first edition in my career before I retired, I can recommend the second edition for professionals in both academic and business areas."

—Lloyd M. Robeson, *Air Products and Chemicals, Inc. (Ret.)*

"Overall, this new text is very readable and well planned. ...a very good introduction to the majority of the important commonly used classes of industrial thermoplastics."

—Garth L. Wilkes, *Virginia Polytechnic Institute and State University*

This new edition of the bestselling *Handbook of Thermoplastics* incorporates recent developments and advances in thermoplastics with regard to materials development, processing, properties, and applications. With contributions from 65 internationally recognized authorities in the field, the second edition features new and updated discussions of several topics, including

- Polymer nanocomposites
- Laser processing of thermoplastic composites
- Bioplastics
- Natural fiber thermoplastic composites
- Materials selection
- Design and application
- Additives for thermoplastics
- Recycling of thermoplastics
- Regulatory and legislative issues related to health, safety, and the environment

The book also discusses state-of-the-art techniques in science and technology as well as environmental assessment with regard to the impact of thermoplastics. Each chapter is written in a review format that covers:

- Historical development and commercialization
- Polymerization and process technologies
- Structural and phase characteristics in relation to use properties
- The effects of additives on properties and applications
- Blends, alloys, copolymers, and composites derived from thermoplastics
- Applications

Giving thorough coverage of the most recent trends in research and practice, the *Handbook of Thermoplastics, Second Edition* is an indispensable resource for experienced and practicing professionals as well as upper-level undergraduate and graduate students in a wide range of disciplines and industries.



CRC Press
Taylor & Francis Group
an informa business

www.taylorandfrancisgroup.com

6000 Broken Sound Parkway, NW
Suite 300, Boca Raton, FL 33487
711 Third Avenue
New York, NY 10017
2 Park Square, Milton Park
Abingdon, Oxon OX14 4RN, UK

K16775

ISBN: 978-1-4665-7722-0



www.crcpress.com