

# Johannes Karl Fink







## **Porous Plastics**

#### Scrivener Publishing

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

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

## **Porous Plastics**

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This edition first published 2022 by John Wiley & Sons, Inc., 111 River Street, Hoboken, NJ 07030, USA and Scrivener Publishing LLC, 100 Cummings Center, Suite 541J, Beverly, MA 01915, USA © 2022 Scrivener Publishing LLC

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#### Library of Congress Cataloging-in-Publication Data

ISBN 978-1-119-89638-8

Cover image: Pixabay.com Cover design by Russell Richardson

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

Printed in the USA

10 9 8 7 6 5 4 3 2 1

## Contents

Pı	Preface				
1	Mat	erials		1	
	1.1	Styro	por	1	
	1.2	Poroi	as Coordination Polymers	2	
		1.2.1	Multifunctional Pillared-Layer Material	2	
		1.2.2	Porous Coordination Polymer-Ionic Liquid Compos	ite 3	
	1.3	Netw	orks	7	
		1.3.1	Microporous Polymer Networks	7	
		1.3.2	Amorphous Microporous Polymer Networks	7	
	1.4	Rigid	Ladder-Type Porous Polymers	19	
	1.5	Photo	ocatalysts	20	
		1.5.1	Compounds for Photocatalytic Aerobic Oxidation	20	
		1.5.2	Floating Photocatalysts	22	
		1.5.3	Photocatalysts with Side Chains	24	
	Refe	erences		26	
2	Syn	thesis <b>I</b>	Methods	29	
	2.1	Porog	gens	29	
		2.1.1	Polymers and Organic Solvents	29	
		2.1.2	Water as Porogen	31	
		2.1.3	Solid Porogens	31	
	2.2	Livin	g Radical Polymerization	32	
	2.3	Emul	sion Polymerization	32	
		2.3.1	High Internal Phase Emulsion Polymerization	32	
		2.3.2	Microchannel Emulsification	40	
	2.4	Solve	nt-Free Polymerization	41	
	2.5	Suspe	ension Polymerization	43	
	2.6	Multi	stage Polymerization Techniques	45	
	2.7	Azo (	Coupling	46	
	2.8	Preci	pitation Polymerization	46	
	2.9	Micro	ofluidics	47	

vi Contents

		<b>D1</b>	. 1 .	10
	2.10	Photo	catalysis	49
	2.11	Therm	al Drawing	50
	2.12	Biodeg	gradable Foam	53
	2.13	Biocor	npatible Porous Three-Dimensional Polymer Matrices	53
	2.14	Breath	-Figure Method	54
		2.14.1	Effects of the Chemical Structure of Polymers	55
		2.14.2	Coating Layers with Selective Wettability on Filter	
			Papers	56
	2.15	Supera	absorbent Polymers	57
	2.16	Functi	onalization Methods	65
		2.16.1	Thiol-Ene Click Chemistry	65
		2.16.2	Ionic Bond Functionalization	66
		2.16.3	Pore-Size-Specific Functionalization	67
	Refe	rences		67
3	Prop	oerties		73
	3.1	Specia	l Materials	73
		3.1.1	Porous Polymer Pressure Sensors	73
		3.1.2	Crack Propagation Behavior	74
	3.2	Standa	urd Test Methods	74
		3.2.1	Polymeric Scaffolds	76
		3.2.2	Leaks in Porous Medical Packaging	77
		3.2.3	Pore Diameter and Permeability	77
		3.2.4	Mercury Intrusion Porosimetry	78
		3.2.5	Pore Size of a Membrane Filter	78
		3.2.6	Computed Tomography	79
		3.2.7	Water Absorption	79
		3.2.8	Microbial Ranking of Porous Packaging Materials	80
		3.2.9	Antibacterial Properties	81
		3.2.10	Performance of Antimicrobials	81
		3.2.11	Surgical Implants	81
		3.2.12	Acoustical Properties	83
		3.2.13	Detection of Leaks in Packaging	84
		3.2.14	Sorbent Performance of Adsorbents	85
	Refe	rences		85
4	Med	ical Us	es	89
	4.1	Medic	al Diagnostics	89
		4.1.1	Extracellular Vesicles	89
	4.2	Medic	al Devices	94
		4.2.1	Stent Grafts	96

		4.2.2	Vascular Grafts	103
	4.3	Medic	al Applications	106
		4.3.1	Porous Polymer Microneedles	106
		4.3.2	Flexible Pressure Sensors	107
		4.3.3	Bone Regeneration	108
		4.3.4	Release of Therapeutic Agents	111
		4.3.5	Implant Dentistry	114
	4.4	Biome	edical Applications	130
		4.4.1	Macroporous Hydrogels	131
		4.4.2	Alginate Foams	132
		4.4.3	Biodegradable Sponges	133
		4.4.4	Biomedical Scaffolds	134
		4.4.5	Biodegradable Electronic Materials	135
		4.4.6	Optical Fibers	136
		4.4.7	Bead Sorbent	137
	Refe	rences		146
5	The	mal In	sulation	153
	5.1	Predic	ction Models	154
	5.2	Radia	tive and Conductive Heat Transfer	155
	5.3	Studie	es of Thermal Conductivity	156
		5.3.1	Macroporous Polymer-Derived SiOC Ceramics	156
	5.4	Poly(e	ethylene) Foams	157
	5.5	Rigid	Foams	157
		5.5.1	Aromatic Polymers	157
		5.5.2	PVC	162
		5.5.3	Poly(urethane)	169
	5.6	Micro	porous Foams	174
		5.6.1	Microporous Poly(styrene)	174
		5.6.2	Conjugate Microporous Foams	175
	5.7	Resilie	ent Porous Polymer Foams	176
	5.8	Electr	ically Conductive Networks	178
		5.8.1	Poly(lactic acid)	178
		5.8.2	Natural Rubber	178
	5.9	Electr	oconducting Polymer Coatings	181
	5.10	Foam	Insulation Structure	182
	5.11	Passiv	e Cooling	185
		5.11.1	Radiative Cooling	186
		5.11.2	Passive Building Cooling	187
	5.12	Sulfur	-Containing Polymers	189
	5.13	Nanoo	cellular Polymers	189

		5.13.1	Poly(methyl methacrylate) Thermoplastic	
			Poly(urethane) Composites	189
		5.13.2	Poly(methyl methacrylate) Multiwalled Carbon	
			Nanotube Composites	190
	5.14	Hous	ehold Applications	191
		5.14.1	Refrigerator	198
	5.15	Fluid	Storage Tank	199
	5.16	Therr	nal Insulation for High Explosives	200
	5.17	Aerog	gels	202
		5.17.1	Polysaccharide-Based Aerogels	202
		5.17.2	Silica Aerogels	203
		5.17.3	Aerogel Fibers	206
	Refe	rences		207
6	Men	nbrane	28	211
	6.1	Cellu	lose Acetate	211
	6.2	Poly(	vinylidene fluoride)	215
		6.2.1	Grafted Phosphonium Poly(vinylidene fluoride)	216
		6.2.2	Hollow Fiber Poly(vinylidene fluoride)	218
		6.2.3	Casting Methods	220
	6.3	Poly(a	amino acid)s	221
	6.4	Нуре	r-crosslinked Polymers	221
	6.5	Mem	brane for Specific Molecular Separation	222
	6.6	Treat	ment of Water	223
		6.6.1	Ammonia Removal	223
		6.6.2	Fine Pore Aeration	224
		6.6.3	Water Contamination Treatment	224
	6.7	Enzyı	me Reactors	240
		6.7.1	Thermoresponsive Enzyme Reactor	240
		6.7.2	Reversible pH-Control	242
		6.7.3	UV-Responsive Enzyme Reactor	244
		6.7.4	Kidney Mimicking	244
	6.8	Electi	rolyte Membranes	246
		6.8.1	Membranes for Fuel Cells	246
	6.9	Mem	branes for Batteries	255
		6.9.1	Membranes for Lithium-Ion Batteries	255
		6.9.2	Membranes for Sodium-Ion Batteries	263
		6.9.3	Vanadium Redox Flow Batteries	265
	6.10	pH-S	ensitive Gating in Membranes	266
	Refe	rences		268

7	Sep	aration	n Methods	275	
	7.1 Chromatography				
		7.1.1	Solid Phase Extraction	275	
		7.1.2	Liquid Chromatography	276	
		7.1.3	Thin-Layer Chromatography	293	
		7.1.4	Gas Chromatography	294	
		7.1.5	Gel Permeation Chromatography	297	
		7.1.6	High-Performance Liquid Chromatography	299	
	7.2	Oil S	pill Control	302	
		7.2.1	Polyolefins	302	
		7.2.2	Porphyrin	303	
		7.2.3	Poly(urethane) Sponge	304	
		7.2.4	Hierarchical Porous Membrane	305	
		7.2.5	Waste Polymers	307	
	7.3	Sorbe	ents	309	
		7.3.1	Purification of Ethylene	309	
		7.3.2	Carbon Dioxide Capture	309	
	7.4	Reco	very of Organic Materials	314	
		7.4.1	Adsorption of Acteoside	314	
		7.4.2	Toxic Organic Materials	316	
		7.4.3	Removal of Organic Micropollutants	319	
		7.4.4	Lysozyme Extraction	326	
	7.5	Meta	l Recovery	328	
		7.5.1	Rice Straw in Poly(urethane) Foams	328	
		7.5.2	Bonding of Metal-Containing Ions	329	
		7.5.3	Porous Porphyrin Polymer	331	
		7.5.4	Iminodiacetic Acid-Functionalized Polymer	340	
		7.5.5	Removal of Toxic Elements	341	
		7.5.6	Polyfunctional Sorbent Materials	342	
	Refe	erences		348	
8	Oth	er Fiel	ds of Use	355	
	8.1	Cerai	mic Articles	355	
	8.2	Polyn	ner-Modified Porous Cement	357	
	8.3	Flam	e Retardant Foams	357	
		8.3.1	Poly(urethane) Foam	357	
	8.4	Clay-	Containing Composites	360	
		8.4.1	Tissue Engineering	360	
		8.4.2	Poly(methyl methacrylate) Composites	360	
		8.4.3	Hectorites	361	

	8.4.4 Catalyst Supports	362
8.5	Lubricant Additives	366
8.6	Cosmetic Compositions	366
8.7	Packaging Materials	367
	8.7.1 Breathable Films	367
8.8	Char Layer	367
8.9	Batteries	368
	8.9.1 Electrodes	368
	8.9.2 Rechargeable Batteries	371
8.10	Light Emission	373
	8.10.1 Porous Conjugated Polymer	373
	8.10.2 Oxacalixarene Macrocycle	375
	8.10.3 Tetraphenylcyclopentadiene	376
	8.10.4 Porous Silicone	376
	8.10.5 Light-Emitting Diodes	377
8.11	Sorbents	378
	8.11.1 Porous Hyper-Crosslinked Polymers	378
Refe	erences	378
Index		381
Acre	onyms	381
Che	micals	386
Gen	eral Index	402

### Preface

Porous polymers are materials that are having pores in their design. Porous polymers are important for various fields of application, as described below. They are used with pores of different sized, i.e. from macropores to micropores.

This book focuses on the issues of porous polymers as well as low molecular compounds that can be introduced in porous polymers.

The book begins with a chapter about polymers that are used for porous materials. Here, among others, microporous polymer networks, hypercrosslinked polymers, and rigid ladder-type porous polymers are detailed. Related issues will also be detailed in the subsequent chapters. In the next chapter, the major synthesis methods for porous polymers are described.

Then, the properties and material testing methods, such as standards, are described in a chapter.

In the following chapters, special fields of applications of porous polymers are described in detail, such as:

Chapter 4: Medical uses, Chapter 5: Thermal insulation, Chapter 6: Membranes, Chapter 7: Separation methods, and Chapter 8: Other fields of use.

The text focuses on the literature of the past decade. Beyond education, this book will serve the needs of industry engineers and specialists who have only a passing knowledge of the plastics and composites industries but need to know more.

#### How to Use This Book

Utmost care has been taken to present reliable data. Because of the vast variety of material presented herein, however, the text cannot be complete in all aspects, and it is recommended that the reader study the original literature for more complete information.

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

#### Index

There are four indices: an index of trademarks, an index of acronyms, an index of chemicals, and a general index.

In the index of chemicals, compounds that occur extensively, e.g., "acetone," are not included at every occurrence, but rather when they appear in an important context.

#### Acknowledgements

I am indebted to our university librarians, Dr. Christian Hasenhüttl, Margit Keshmiri, Friedrich Scheer, Christian Slamenik, Renate Tschabuschnig, and Elisabeth Groß for support in literature acquisition. I also want to express my gratitude to all the scientists who have carefully published their results concerning the topics dealt with herein. This book could not have been otherwise compiled.

Last, but not least, I want to thank the publisher, Martin Scrivener, for his interest in publishing this book. In addition, my thanks go to Jean Markovic, who made the final copyedit with utmost care.

> Johannes Fink Leoben, May 2022

# 1

## **Materials**

Porous materials are typically categorized into three classes that have different pore sizes (1):

- 1. Macroporous with pore diameter larger than 50 nm,
- 2. Mesoporous (pore diameter between 2 nm and 50 nm), and
- 3. Microporous materials (pore diameter smaller than 2 *nm*).

While conventional polymer networks undergo pore collapse upon solvent removal as polymer strands can adopt many conformations in order to pack space efficiently, recent research efforts have popularized several classes of polymer networks that possess permanent porosity based on the use of rigid components.

#### 1.1 Styropor

Otis Ray McIntire (1918-1996), a chemical engineer at Dow Chemical, rediscovered a process first patented by Swedish inventor Carl Munters (2).

According to the Science History Institute, "Dow bought the rights to the Munters method and began producing a lightweight, water-resistant, and buoyant material that seemed perfectly suited for building docks and watercraft and for insulating homes, offices, and chicken sheds (3). In 1944, Styrofoam was patented.

Before 1949, chemical engineer Fritz Stastny (1908-1985) developed pre-expanded poly(styrene) beads by incorporating aliphatic hydrocarbons such as pentane. These beads are the raw material for molding parts or extruding sheets. BASF and Stastny applied for a patent that was issued in 1949. The molding process was demonstrated at the Kunststoff Messe in Düsseldorf in 1952. These products were named Styropor (3).

The crystal structure of isotactic poly(styrene) was reported by Giulio Natta (4). In 1954, the Koppers company in Pittsburgh, Pennsylvania, developed expanded poly(styrene) foam under the trade name Dylite (5).

### 1.2 Porous Coordination Polymers

The design, analysis and applications of coordination polymers have been descried in a monograph (6).

A coordination polymer is an inorganic or organometallic polymer structure containing metal cation centers linked by ligands. More formally, a coordination polymer is a coordination compound with repeating coordination entities extending in 1, 2, or 3 dimensions (7, 8)

Examples of coordination polymers are lanthanoid coordination polymers, organometallic networks, and organic-inorganic hybrids (6).

#### 1.2.1 Multifunctional Pillared-Layer Material

A multifunctional pillared-layer porous coordination polymer, has been constructed based on a flexible viologen derivative, 1,1'-bis(4-carboxybenzyl)-4,4'-bipyridinium dichloride, and an oxalate co-ligand. 1,1'-Bis(4-carboxybenzyl)-4,4'-bipyridinium dichloride is shown in Figure 1.1.



Figure 1.1 1,1'-Bis(4-carboxybenzyl)-4,4'-bipyridinium dichloride.

Single-crystal X-ray analysis showed that the compound possesses multichannels with dimensions of about  $6.1 \times 6.6$  Å along the [110] and [-110] directions and  $4.2 \times 7.6$  Å along [100], and a void space of about 41.4%.

Hydrogen adsorption measurements at 77 *K* and 1 *atm* indicated that the compound exhibits a hydrogen uptake of 0.71%. Owing to the incorporation of bipyridinium acceptor units, the compound can selectively accommodate aromatic donors into its nano-sized pores based on charge-transfer interactions in an elastic way, and afford a specific color to different guests.

Furthermore, the effect of perturbation exerted by the guest molecules on its magnetic properties has been investigated. The results indicated that the donor inclusion has little effect on its antiferromagnetic behavior, whereas dehydration of the compound decreases the strength of the magnetic exchange couplings and results in a change of the antiferromagnetic transition temperature from 14.7 *K* to 9.8 *K* (9).

#### 1.2.2 Porous Coordination Polymer-Ionic Liquid Composite

A porous coordination polymer-ionic liquid composite has been described that includes an insulating structure composed of a porous coordination polymer, and an ionic liquid retained inside pores of the porous coordination polymer. The porous coordination polymer preferably has a main chain containing a typical metal element (10).

It has been proposed to apply an ionic liquid owing to high ionic conductivity thereof to an electrochemical device as an electrolyte for a battery or an electrical double-layer capacitor. The ionic liquid has extremely high flame retardance, and hence when used as the electrolyte for the electrochemical device, there is no need for a combustible organic solvent, thus ensuring the electrochemical device with high safety (10).

A schematic diagram that shows that an ionic liquid is filled with particles of the porous coordination polymer to form particles after filling is shown in Figure 1.2.

Here a a plurality of particles 111 composed of a porous coordination polymer are filled with a ionic liquid 12. The composite 131 obtained by a molding process. The structure 11, which is used as an electrolyte for a battery or an electrical double-layer capacitor,



**Figure 1.2** Synthesis of a porous coordination polymer-ionic liquid composite (10).

has a dense structure, thus making it easier for ion conduction pathways between the particles to be connected to each other. Hence, the composite 131 is a satisfactory ion conductor. In the case of using the structure 11 obtained by subjecting a plurality of the particles 111 composed of the porous coordination polymer to compression molding, a plurality of voids are respectively formed between the particles 111 of the porous coordination polymer (10).

Examples of the porous coordination polymer are collected in Table 1.1.

Compound		Shortcut
Zn(MeIM)2		ZIF-8
Al(OH)[BDC]		MIL-53(A1)
Cr(OH)[BDC]		MIL-53(Cr)
Fe(OH) [BDC]		MIL-53(Fe)
Zn2 (DOBDC)		MOF-74(Zn)
Mg2 (DOBDC)		MOF-74(Mg)
Al(OH)(1,4-NDC)		-
Cr3F(H2O)2O(BD	C)3	MIL-101(Cr)
Al8(OH)12(OH)3(	(H2O)3 [BTC]3	MIL-110(Al)
Abbreviation	Compound	
HMeIM	2-Methylimida	zole
H2BDC	1,4-Benzenedicarboxylic acid	
H4DOBDC	2,5-Dihydroxyterephthalic acid	
H2NDC	1,4-Naphthalei	nedicarboxylic acid
H3BTC	1,3,5-Benzenet	ricarboxylic acid
H2BPDC	4,4'-Biphenyld	icarboxylic acid
H2TPDC	4,4"-p-Terphen	yldicarboxylic acid

Table 1.1 Porous coordination polymers (10).

The acids in Table 1.1 are shown in Figure 1.3.

Examples of hard acids, hard bases, soft acids, soft bases, intermediate acids, and intermediate bases are described in a monograph (11).



2-Methylimidazole





1,4-Benzenedicarboxylic acid









1,3,5-Benzenetricarboxylic acid

4,4'-Biphenyldicarboxylic acid



4,4"-p-Terphenyldicarboxylic acid

Figure 1.3 Acids in Table 1.1.

#### 1.3 Networks

#### 1.3.1 Microporous Polymer Networks

Microporous materials are defined as materials containing interconnected pores of less than 2 nm in diameter (12)

Due to their large surface area, many conventional microporous materials, such as zeolites and activated carbons, are widely used as catalysts, sorbents, and separation membranes. Recently, the field has evolved rapidly with the development of several novel types of microporous polymer networks. These materials not only benefit fundamental research by introducing modular approaches to accessing numerous sophisticated structures, but also provide new opportunities for various emerging applications (1).

The central design principle for introducing permanent microporosity into polymer networks involves the use of rigid building blocks. Such rigidity precludes the network strands from behaving effectively as entropic molecular springs and prevents the collapse of microporous structures upon solvent removal; consequently, the mechanical properties of these materials are stiff yet brittle.

Furthermore, the rigidity of the monomers prevents small loop formation and allows for establishing long-range order in the presence of self-error-correcting mechanisms, e.g., a reversible bond formation (1).

So, microporous polymer networks can be either amorphous or crystalline. Aside from the general use of very rigid components, the basic concepts of microporous polymer network synthesis are similar to those discussed above for either covalent or physical polymer networks.

#### 1.3.2 Amorphous Microporous Polymer Networks

Amorphous microporous polymer networks of different types have been denoted by various names, such as:

- 1. Polymers with intrinsic microporosity (PIMs) (13),
- 2. Porous organic polymers (POPs) (14),
- 3. Conjugated microporous polymers (CMPs) (15), and
- 4. Hyper-crosslinked polymers (16).

It has been suggested to divide these materials into two categories, based on whether or not the strands are covalently crosslinked (1).

#### 1.3.2.1 Conjugated Microporous Polymers

Conjugated microporous polymers (CMPs) are a class of organic porous polymers that combine *p*-conjugated skeletons with permanent nanopores, in sharp contrast to other porous materials that are not *p*-conjugated and with conventional conjugated polymers that are nonporous. As an emerging material platform, CMPs offer a high flexibility for the molecular design of conjugated skeletons and nanopores.

A lot of chemical reactions, building blocks and synthetic methods have been developed and a broad variety of CMPs with different structures and specific properties have been synthesized, driving the rapid growth of the field. CMPs are unique in that they allow the complementary utilization of *p*-conjugated skeletons and nanopores for functional exploration; they have shown great potential for challenging energy and environmental issues, as exemplified by their excellent performance in gas adsorption, heterogeneous catalysis, light emitting, light harvesting and electrical energy storage. This review describes the molecular design principles of CMPs, advancements in synthetic and structural studies and the frontiers of functional exploration and potential applications.

Building blocks with different geometries are listed in Table 1.2.

The structures of some building blocks with different geometries, sizes and reactive groups for the synthesis of CMPs are shown in Figure 1.4.

To construct a conjugated skeleton, the synthetic reaction must covalently link the building blocks with a *p*-conjugated bond.

The chemical reactions utilized for the preparation of linear conjugated polymers can also be employed for the synthesis of CMPs. The special reactions are listed in Table 1.3 and are shown in Figure 1.5.

Because building blocks can have different geometries, reactive groups, and P systems, this structural diversity significantly enhances the flexibility of the design of both skeletons and pores. **Table 1.2** Building blocks with different ge-ometries (15).

C2 Compounds 1,4-Dibromobenzene 1,2-Dibromobenzene 1,4-Dibromo-2-methyl-benzene 1,4-Dibromo-2-trifluoromethyl-benzene 2,5-Dibromofluorobenzene 1,4-Dibromo-2-nitro-benzene 4,7-Dibromo-2,1,3-benzothiadiazole 2,5-Dibromo pyridine 2,5-Dibromobenzoic acid 2,5-Dibromonitrobenzene 1,4-Dibromo-2,5-difluorobenzene 1,4-Dibromo-2,5-dimethylbenzene 1,4-Dibromo-2,5-dihydroxybenzene 1,4-Dibromo-2,5-dimethoxybenzene 1,3-Dibromobenzene 2,6-Dibromophenol 2,4-Dibromoaniline 2,6-Dibromoaniline 3,5-Dibromo pyridine 3,5-Dibromo-N,N-dimethyl-4-pyridinamine 2,7-Dibrom-9H-carbazol 1,6-Dibromo-2-naphthol 2,6-Dibromonaphthalene 9,10-Dibromoanthracene 4,4'-Dibromobiphenyl 5-Bromo-2-(4-bromophenyl)pyridine 5,5'-Dibromo-2,2'-bipyridine 4,4'-Dibromooctafluorobiphenyl 1,4-Diiodobenzene 4,4'-Diiodobiphenyl 1,4-Diaminobenzene 4,4'-Diaminobiphenyl 1,2-Dicyanobenzene 1,3-Dicyanobenzene 1,4-Dicyanobenzene 4,4'-Diacyanobiphenyl 1,1':4',1"-Terphenyl-4,4"-dicarbonitrile

## **Table 1.2 (cont)** Building blocks with different geometries(15).

C3 Compounds

1,3,5-Tribromobenzene

1,3,5-Tris(3-bromophenyl)benzene

1,3,5-Tris(4-bromophenyl)benzene

2,4,6-Tris(p-bromophenyl)-s-triazine

1,3,5-Tris(4-bromophenylethynyl)benzene

1,3,5-Tris(4-aminophenyl)benzene

C4 Compounds

1,2,4,5-Tetrabromobenzene

1,3,6,8-Tetrabromopyrene

1,3,6,8-Pyrenetetracarbaldehyde

1,2,4,5-Tetraaminobenzene

2,2',7,7'-Tetrabromo-9,9'-spirobifluorene

2,2',7,7'-Tetraamino-9,9'-spirobifluorene

1,1',1"',1"'-(1,1,2,2-Ethenetetrayl)tetrakis (4-bromobenzene)

C6 Compounds

1,2,3,4,5,6-Hexabromobenzene

1,2,3,4,5,6-Hexakis(4-bromophenyl)benzene

**Table 1.3** Reactions for preparation of conjugat-<br/>ed polymers.

Reaction name	References
Suzuki cross coupling reaction	(17, 18)
Yamamoto reaction	(19, 20)
Sonogashira-Hagihara reaction	(21, 22)
Oxidative coupling reaction	(23–25)
Schiff base reaction	(26–28)
Friedel-Crafts reaction	(29)
Phenazine ring fusion reaction	(30)
Cyclotrimerization	(31, 32)



1,4-Dibromobenzene





1,2-Dibromobenzene



1,4-Dibromo-2-trifluoromethylbenzene



2,5-Dibromofluorobenzene



1,4-Dibromo-2-nitro-benzene

4,7-Dibromo-2,1,3-benzothiadiazole



2,5-Dibromo pyridine



2,5-Dibromonitrobenzene

1,4-Dibromo-2,5-difluorobenzene

Figure 1.4 Building blocks (15).





2,5-Dibromobenzoic acid







1,4-Dibromo-2,5-dimethylbenzene



2,4-Dibromoaniline



3,5-Dibromo-N,N-dimethyl-4-pyridinamine



2,7-Dibromo-9H-carbazole



2,6-Dibromonaphthalene



1,3-Dibromobenzene

3,5-Dibromo pyridine



1,4-Dibromo-2,5-dihydroxy benzene



1,6-Dibromo-2-naphthol









4,4'-Dibromobiphenyl



5-Bromo-2-(4-bromophenyl)pyridine



5,5'-Dibromo-2,2'-bipyridine

4,4'-Dibromooctafluorobiphenyl





1,4-Diaminobenzene 1,2-Dicyanobenzene

1,4-Dicyanobenzene



1,1':4',1"-Terphenyl-4,4"-dicarbonitrile

#### 14 Porous Plastics



#### 1,3,5-Tribromobenzene



#### 1,3,5-Tris(3-bromophenyl)benzene



2,4,6-Tris(*p*-bromophenyl)-*s*-triazine



1,3,5-Tris(4-bromophenylethynyl)benzene



1,3,5-Tris(4-aminophenyl)benzene

#### 16 Porous Plastics



1,3,5-Tris(4-cyanophenyl)benzene



1,3,6,8-Pyrenetetracarbaldehyde



1,1',1",1"'-(1,1,2,2-Ethenetetrayl)tetrakis (4-bromobenzene)