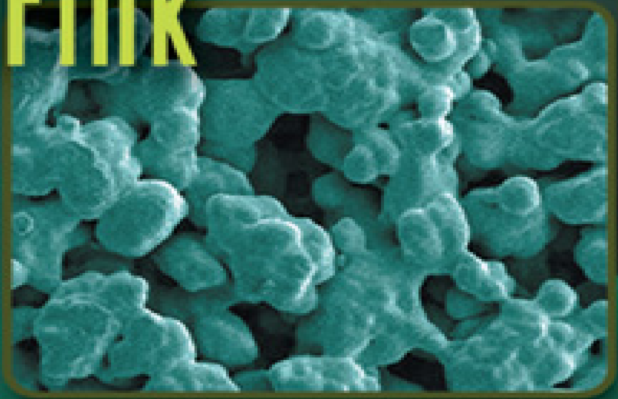
POROUS PLASTICS

Johannes Karl Fink



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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, hyper-crosslinked 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.

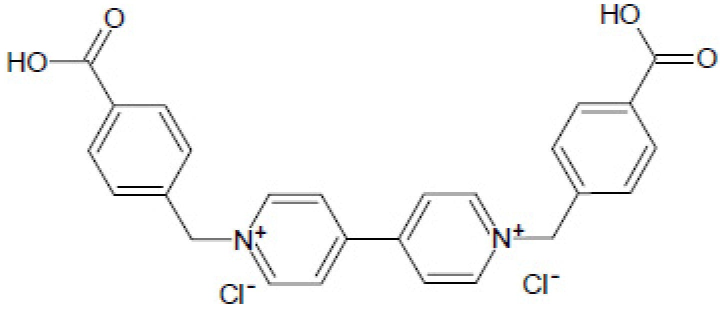


Figure 1.1 1,1’-Bis(4-carboxybenzyl)-4,4’-bipyridinium dichloride.

Single-crystal X-ray analysis showed that the compound possesses multichannels with dimensions of about 6.1×6.6 Å along the [110] and [-110] directions and 4.2×7.6 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, 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).

in Table 1.1.

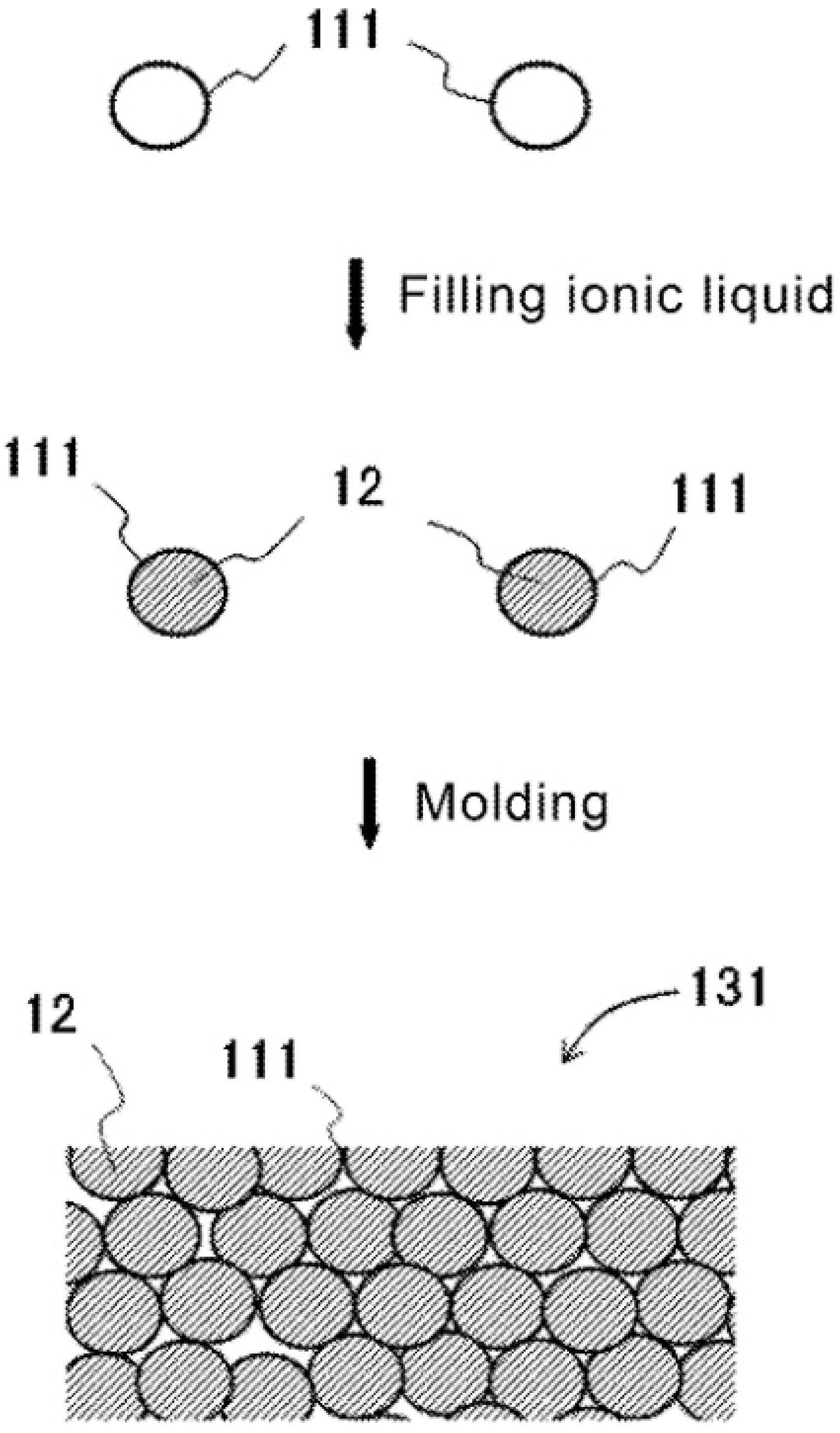


Figure 1.2 Synthesis of a porous coordination polymer-ionic liquid composite (10).

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

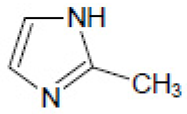
Table 1.1 Porous coordination polymers (10).

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(BDC)3	MIL-101(Cr)
Al8(OH)12(OH)3(H2O)3 [BTC]3	MIL-110(Al)

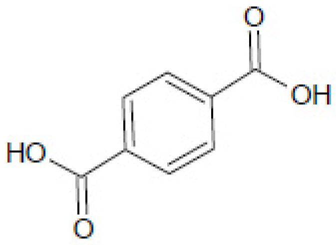
Abbreviation	Compound
HMeIM	2-Methylimidazole
H2BDC	1,4-Benzenedicarboxylic acid
H4DOBDC	2,5-Dihydroxyterephthalic acid
H2NDC	1,4-Naphthalenedicarboxylic acid
H3BTC	1,3,5-Benzenetricarboxylic acid
H2BPDC	4,4’-Biphenyldicarboxylic acid
H2TPDC	4,4”-*p*-Terphenyldicarboxylic acid

The acids in Table 1.1 are shown in Figure 1.3.

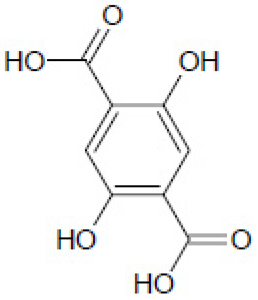
Examples of hard acids, hard bases, soft acids, soft bases, intermediate acids, and intermediate bases are described in a monograph (11).



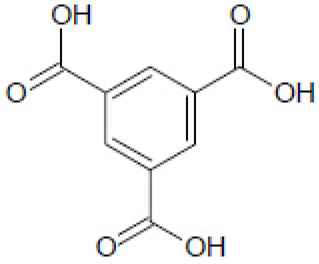
2-Methylimidazole



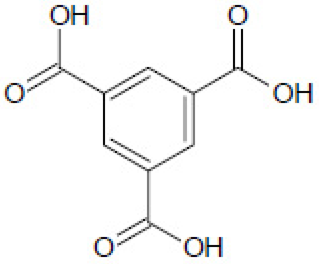
1,4-Benzenedicarboxylic acid



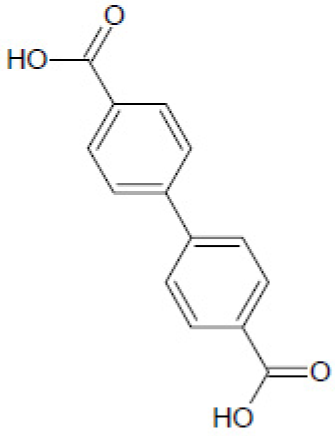
2,5-Dihydroxyterephthalic acid



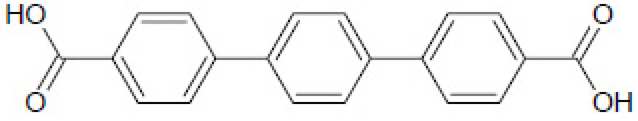
1,4-Naphthalenedicarboxylic acid



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