

The Chemistry of Porous Polymers: The Holy Grail

Michael S. Silverstein^[a]

Dedicated to Professor Krzysztof Matyjaszewski on his 70th birthday and on the 25th anniversary of “Controlled/Living Radical Polymerization”, in profound appreciation for his support and friendship.

Abstract: Porous polymers have been evolving continuously since the introduction of foam rubber in 1929. Today, pore diameters ranging from sub-nanometre to millimetre can be generated controllably. Cutting-edge porous polymers are now being applied at the forefront of critical problems with societal and environmental impact including advanced systems for biomedicine, water purification, energy storage, and gas purification and storage. The commonly-used pore generation approaches include macromolecular design, self-

assembly, phase separation, solid and liquid templating, sol-gel formation, and foaming. In each, *The Chemistry of Polymers*, both the polymerization chemistry and the macromolecular structural chemistry, must be applied advantageously to generate the empty volume within the polymer and then fix it in place. This essay will traverse the various pore size scales, describing the chemistries involved and discussing their implications.

Keywords: Polymers · Microporous materials · Mesoporous materials · Macroporous materials · Macromolecules

1. Introduction: Much Ado about Nothing

Porous polymers, when using a broad, all-encompassing definition, describes polymers that contain *pores*, small empty volumes or spaces (where *small*, in this broad definition, can be diameters ranging from sub-nanometre to millimetre). The challenge in porous polymers is to generate the empty volume and then fix it in place. The phrase *The Chemistry of Polymers* contains a duality in meaning with interesting implications. In essence, *The Chemistry of Polymers* can be used to describe the polymerization chemistry, and in addition, to describe the chemistry of the resulting macromolecular structure. Both facets of *The Chemistry of Polymers* are of paramount importance for the successful generation of porous polymers. The generation and fixation of pores usually involves both the wide-ranging toolbox of polymerization reactions and the wide-ranging toolbox of macromolecular structures. Polymer foams, with millimetre-scale pores, can be generated by gas evolution during polymer synthesis or by gas evolution during polymer processing. Microporous polymers, with sub-nanometre-scale pores, can be generated by the formation of framework structures during polymer synthesis or by the formation of hypercrosslinked networks during post-synthesis processing. This essay will explore *The Chemistry of Polymers* through the prism of porous polymers, and more specifically, through the approaches used to generate micropores, mesopores, and macropores.

The International Union of Pure and Applied Chemistry (IUPAC) has defined three pore-size classifications: *micropores* (less than 2 nm), *mesopores* (between 2 and 50 nm), and *macropores* (greater than 50 nm) – the term *nanopore* can be applied to all three IUPAC pore-size classifications.

2. Background: Don't Know Much about History, Don't Know Much Chemistry

The 1920 Staudinger “On Polymerization” article insightfully described the nature of the chemical structure in molecules produced by polymerization reactions.^[1] Staudinger intuited that these molecules consisted of covalently bonded entities with exceptionally high molecular weights, rather than colloidal assemblies of low molecular weight entities held together by weaker bonds. Staudinger’s insights came after Bayer AG, in 1909, began industrial production of synthetic rubber (polyisoprene). The introduction of synthetic rubber was a response to the increasing demand for the air-filled, pneumatic, rubber tires that were introduced in the 1890s. The advantageous combination of polymers and air that began with the introduction of rubber tires continued with the introduction of foam rubber. A rubber foam with a “sponge-like or cellular structure from aqueous emulsions or dispersions”^[2] was produced by Dunlop Rubber in 1929, using whipping to successfully entrain millimetre-scale air bubbles into a latex before it “set”.^[2–4] This breakthrough in foam production paved the way for a multitude of innovative polymer foams, both rubbery and stiff, whose development paralleled the development of the polymers themselves, including polystyrene (PS, 1931), polyurethane (1937), and polyethylene

[a] M. S. Silverstein
Department of Materials Science and Engineering
Technion – Israel Institute of Technology
Haifa 32000, Israel
Fax: +972-77-887-1797
E-mail: michael@technion.ac.il

(1941).^[5] These families of polymer foams combined pore generation processes (physical entrainment, chemical reactions, and/or evaporation) with “setting” processes (polymerization, crosslinking, and/or reducing the polymer mobility through cooling).

The ability to generate pore-filled polymers has led to a multitude of applications including membranes and polymer absorbents-adsorbents. Porous polymer membranes based on nitrocellulose (“collodion”), first mentioned by Fick in 1855, were evaluated for dialysis. Membranes produced using a non-solvent-induced phase separation (NIPS, immersing a solution-cast film in water during solvent evaporation) were introduced by Bechhold in 1907.^[6–7] NIPS was able to successfully produce micrometre-scale pores by ensuring that “the gradual diminution in size of the interstices [pores] in collodion may be stopped”. The breakthrough Loeb-Sourirajan phase separation process, introduced in the early 1960s, produced defect-free, asymmetric reverse osmosis cellulose membranes consisting of an ultrathin, selective film (high flux) on a porous support (mechanical strength) making industrial-scale production and application practical.^[8–9] These examples demonstrate that it can take decades to find the right combination of polymerization, macromolecular structure, and processing to achieve feasibility for industrial application.

3. Approaches: How to Make Holes and Influence Porosity

Some approaches to pore generation involve the polymerization chemistry, some involve the macromolecular structural chemistry, and some involve both.^[10–12] The continually-expanding toolbox of polymerization reactions is constantly providing new ways to synthesize macromolecules and to produce novel macromolecular architectures. The macromolecular structural chemistry influences the macromolecule’s interactions with its environment (e.g. solvents, non-solvents, other polymers). These interactions have been described by the Flory-Huggins interaction parameter, which in turn, has been related to the difference in the solubility parameters ascribed to the polymer and the solvent. The solubility parameter, in turn, has been directly related to the polymer’s macromolecular structure through the chemical group attraction constants compiled by Small and Hoy.^[13] The availability

of a wide variety of polymerization chemistries and a wide variety of macromolecular structural chemistries provides access to an unlimited number of porous polymer possibilities.

The pore generation methodology is usually intrinsically connected to the size-scale of the resulting pores. The commonly used approaches to pore generation can be categorized (in an extremely non-rigorous manner) as: macromolecular design, self-assembly, phase separation, solid and liquid templating, sol-gel formation, and foaming.

Macromolecular design. Microporous structures can be generated *a priori* through the design of relatively rigid macromolecular structures. Pores can be generated either by the manner in which the monomers are designed to assemble during polymerization (e.g. covalent organic frameworks (COFs), conjugated microporous polymers (CMPs), covalent triazine frameworks (CTFs), and porous aromatic frameworks (PAFs)) or by the manner in which stiff, twisted macromolecules pack during processing (e.g. polymers of intrinsic microporosity (PIMs)). In addition, pores can also be generated by *locking-in* the structure of a swollen polymer (e.g. hypercrosslinking).^[12,14–15]

Self-assembly. Mesoporous structures can be generated by the spontaneous self-assembly of large molecules containing sections that are incompatible.^[16] The self-assembly of surfactant molecules containing a hydrophilic head, a hydrophobic tail, and a polymerizable group can be used to produce porous structures (hexagonal or cubic) that can then be transformed into porous polymers through polymerization. The self-assembly of block copolymers (BCPs) into cylindrical or gyroidal structures can be used to produce porous polymers by using a block or a block-linker that can be subsequently removed (e.g. through etching).

Phase separation. Micrometre-scale porous structures, most commonly used for membranes, are generated by controlling the polymer-solvent miscibility, and thus, the phase separation and the fixation of the phase separated structure (e.g. NIPS and solvent induced phase separation (SIPS)).^[17] Interestingly, Staudinger mentioned both SIPS and NIPS in his ground-breaking 1920 article “On Polymerization”.^[1]

Solid and Liquid Templating. Micrometre-scale to millimetre-scale porous structures are generated around a removable solid or liquid templating structure (e.g. salt leaching, particle templating, emulsion templating) and fixed through polymerization (for monomers) or solvent removal (for polymer solutions).



Michael S. Silverstein holds the Sherman – Gilbert Chair in Energy at the Department of Materials Science and Engineering, Technion – Israel Institute of Technology, which he joined in 1989. He is the Chairman of the Technion’s Interdepartmental Program in Polymer Engineering and an Honorary Fellow of the Israel Polymers and Plastics Society. He is presently investigating a plethora of novel emulsion-templated polymers and has developed an array of extraordinary materials including porous superabsorbent and adsorbent hydrogels, liquid-droplet-filled monoliths for storage and release, porous shape memory polymers, and carbons with hierarchical porosities. Silverstein received an Honours B.A.Sc. in Engineering Science from the University of Toronto in 1983, received a D.Sc. from the Technion in 1988, working with Prof. Moshe Narkis, and spent a year as a Postdoctoral Research Associate at Case Western Reserve University, working with Professors Eric Baer and Anne Hiltner.

Sol-Gel Formation. Micrometre-scale to millimetre-scale porous structures are generated by gel formation that is followed by solvent removal (e.g. hydrogels, organogels).

Foaming. Millimetre-scale pores are generated through gas generation and expansion (e.g. low boiling point solvents, the products of chemical reactions) and fixed through polymerization, crosslinking, and/or reducing the polymer mobility through cooling.

This *Essay* will traverse various porous polymer size scales and assess how the polymerization chemistries and the macromolecular structural chemistries enable the generation of porous polymers through three representative processes: macromolecular design, block copolymer self-assembly, and emulsion templating. Some porous polymer applications that have significant societal and/or environmental impact will be discussed.

4. Macromolecular Design: A Hole in One

The challenges in accessing microporosity include the extremely high polymer-polymer cohesive forces that exists between the pore surfaces when they are less than a nanometre apart and the extremely high solvent-removal capillary forces during synthesis, both of which can drive pore elimination through structural collapse. The macromolecular structures of microporous polymers, therefore, must be designed from rigid elements that are able to resist such forces. Crosslinked polystyrene networks, described by Staudinger in the 1930s,^[18] are used for adsorption, separation, ion-exchange, and solid-phase synthesis applications (e.g. Merrifield resins).^[19] Microporous hypercrosslinked PS with extremely small pore diameters (<2 nm) and high specific surface areas (>1000 m²/g) was introduced by Danankov in 1973 (the specific surface area indicates the extents of microporosity and mesoporosity).^[20–21] Hypercrosslinking accesses microporosity by *locking-in* the swollen state of polymer networks (e.g., via a Friedel-Crafts reaction) followed by solvent removal. Such microporous polymers have exhibited great potential for gas adsorption, separation processes, energy storage, and catalysis. Unfortunately, hypercrosslinking reactions are limited to styrenics and a few other polymers and the control over the pore size and the pore volume is relatively limited.

The concept of using the macromolecular design of polymers for adsorption applications began in the mid-1990s with Yaghi's introduction of metal organic frameworks (MOFs), which consist of organic ligands coordinated to metal ions.^[22–23] Since then, a wide variety of high-porosity polymer families, both amorphous and crystalline, have been introduced.^[10,14,24–26] In the late 2000s, extensive libraries of network systems (e.g. COFs,^[27] CMPs,^[28] CTFs,^[29] PAFs^[30]) and of linear systems (e.g. PIMs^[31]) were developed, as illustrated schematically in Figure 1.

Superior control over the macromolecular structure, and hence the pore size and volume, was initially enabled using step growth polymerization (SGP) to synthesize two dimen-

sional, crystalline COFs (illustrated schematically in Figure 1a). The rigid COF building blocks were originally linked into two dimensional ordered structures with relatively few faults using reversible, and therefore self-repairing, boroxine linkers (boric acid self-condensation) and boronate ester linkers (co-condensation with a rigid, hydroxyl-bearing linker). Since the boron-containing linkages are relative unstable (hydrolytically and oxidatively), the macromolecular design of COFs with more robust linkage chemistries (e.g., amines, imines, other nitrogen-containing groups) was achieved using a judicious choice of monomers, broadening the available porous structures and enhancing their applicative practicality.^[32] A wide variety of conceptually similar polymerization chemistries was then applied to generate innovative, pre-designed, rigid macromolecular structures that could successfully access microporosity.^[32]

Another approach to accessing microporosity through macromolecular design involves using rigid, three dimensionally contorted monomers (e.g., spirobifluorene) to synthesize rigid, twisted, networks which are not able to pack efficiently, thus entrapping empty volume (illustrated schematically in Figure 1b). The long list of SGPs used to synthesize rigid, twisted, microporous networks include Sonogashira-Hagihara coupling for CMPs, Yamamoto coupling for PAFs, and a variety of coupling, click, and cyclotrimerization reactions.^[10] PIMs are microporous polymers with rigid, contorted linear macromolecules (as opposed to networks) that are, therefore, processable (illustrated schematically in Figure 1c).

The use of microporous polymers in applications with societal and/or environmental impact has demonstrated significant potential. Unfortunately, while macromolecular design can be used to synthesize microporous polymers with a wide range of possible chemical structures, they are usually limited to powders. On the other hand, the chemical structures of microporous polymer monoliths are, for the most part, limited to hypercrosslinked styrenics. One critical challenge for future development is the successful generation of polymer monoliths with accessible microporosities and chemical structures that can be tuned via macromolecular design. Achieving both these objectives will lead to a transformative enhancement in the prospects for practical application.

5. Self-Assembly: An Ace in the Hole

A wide variety of mesoporous polymers have been generated using various polymerization reactions to synthesize BCPs with advantageous etching-solubility behaviors.^[10] A few representative pore-generation processes are illustrated schematically in Figure 2. BCP-generated mesoporous polymer films can be applied as membranes, as lithographic masks, and as templates for the generation of inorganic mesoporous materials. The growing number of polymers available, the growing number of mesoporous structures available, and the enhancements in the ability to achieve “structural perfection”

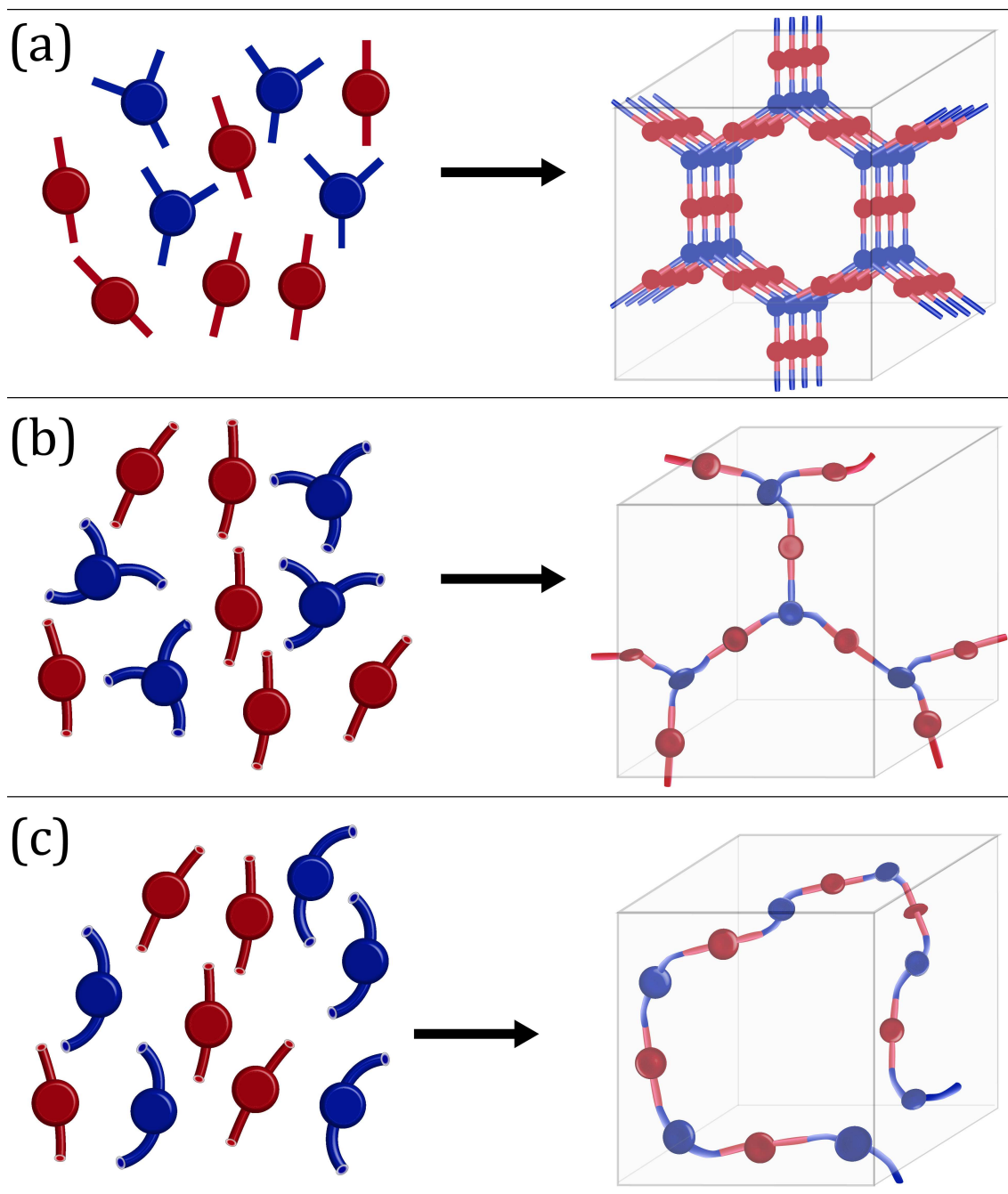


Figure 1. A schematic illustration describing the structures of microporous polymers generated through macromolecular design: (a) two dimensional COFs; (b) three dimensional amorphous networks; (c) linear PIMs.

has enhanced the potential for the adoption of BCP-based mesoporous polymers for industrial application.

Self-assembling BCPs with narrow molecular weight distributions can be synthesized using a variety of polymerization chemistries, with the most common consisting of anionic polymerization and controlled radical polymerizations. In these “living” polymerizations, sequential monomer addition is usually used to “grow” one block from another.

Macromolecules that cannot be synthesized using a “living” reaction can be incorporated into BCPs by attaching radical-initiating groups at their end(s). The resulting “macroinitiators” can then be used as anchors for “growing” additional blocks. As described above for *Macromolecular Design*, the macromolecular structural chemistry is critical. Thermodynamically, blocks of incompatible polymers are driven to phase separate, often into ordered structures, to minimize

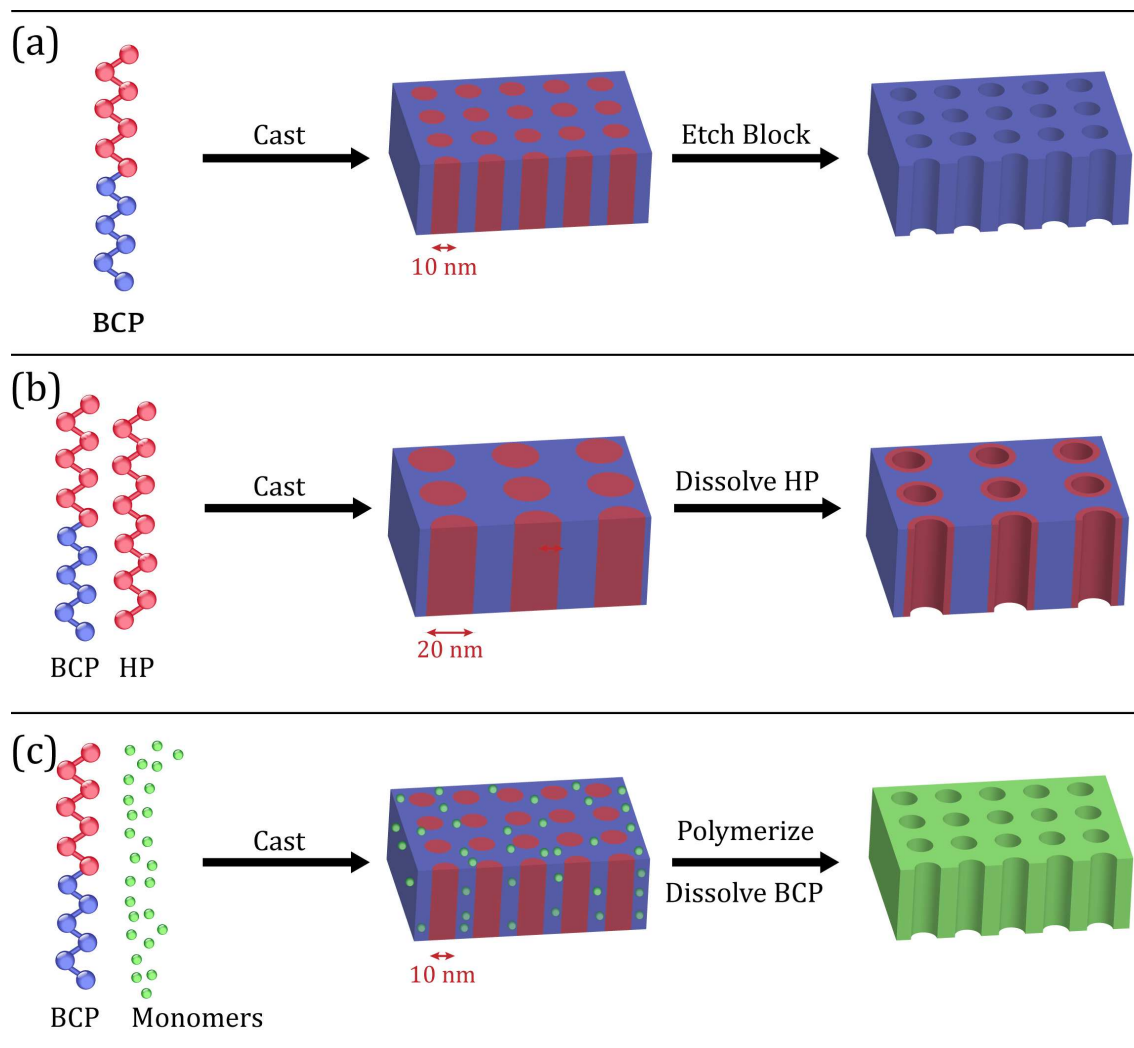


Figure 2. A schematic illustration describing the synthesis of mesoporous polymers through BCP self-assembly: (a) block removal; (b) additive (e. g., HP) removal; (c) polymerization and BCP removal.

polymer-polymer interface. Phase diagrams that include spherical, cylindrical, gyroidal, and lamellar phases have been generated for diblocks, ABA triblocks, and ABC triblocks. These diagrams present the microphase-separated structures as functions of the composition, the molecular weight, and the Flory-Huggins interaction parameter.^[33–35] The self-assembly process and the resulting structure can be driven by temperature, solvent evaporation, and/or the addition of a non-solvent.

The size of the microphase-separated domains in BCPs, limited by the covalent links between the blocks, is usually on the order of 10 nm. Porous structures have been generated from a long list of self-assembled BCP structures through a combination of etching, dissolution, and physical reconstruction.^[10,36–41] The popularity and ease of using BCP self-assembly to generate mesoporous structures reflects the spontaneous nature of the phase separation, the ability to controllably design ordered (cylindrical) or bicontinuous

(gyroidal) structures (through block composition, molecular weight, and compatibility), and the ability to refine the structure (through solvent and/or thermal annealing).^[10,42] Access to the gyroidal structure (two phase-separated, continuous phases that are intertwined) is especially important for generating continuous mesoporosity. The resulting mesoporous polymers have been used as templates for the generation of mesoporous metals, ceramics, and carbons.^[39,43–49] In addition, mesoporous polymers with cylindrical structures can be used as membranes, as “lithographic” masks, and as templates for generating nanometre-scale dot and pillar structures.^[46,48,50–53] The different approaches used for generating mesoporous polymer structures from the self-assembled BCPs can be loosely categorized as: block removal, additive removal, and BCP removal.

Block Removal. One of the blocks is removed selectively, leaving the other blocks as the structural framework (illustrated schematically in Figure 2a). Selective etching can be

used to remove a block that was specifically incorporated into the BCP based on its propensity to degrade with relative ease (e.g., poly(lactic acid)). Incorporating an etchable or degradable block-linker (e.g., oligomeric poly(methyl methacrylate)) into the BCP is an elegant variation on this approach. In an ABC copolymer containing B as a degradable block-linker, the A and C blocks are chosen for their ability to form a well-defined microphase-separated structure and for their selective solubilities (solvents for C do not dissolve A and vice versa). Once the B block has been removed, one of the two endblocks can then be removed through selective dissolution.^[40] For both methods, the framework polymer must be robust enough to withstand the pore generation process without collapsing. Therefore, the framework polymers are usually glassy, cross-linked, and/or crystalline.

Additive Removal. An additive that is preferentially located in one of the blocks is removed, leaving the now porous BCP in place (illustrated schematically in Figure 2b). The additive, which is only miscible in one of the blocks, acts as a porogen. This additive can be a low molecular weight molecule or a homopolymer (HP) whose macromolecular structure matches that of one of the blocks. A selective solvent for the block in which the additive is located can be used to remove the additive, leaving the additive-containing block on the pore surface. A related porosity-generating process involves reconstructing the microphase-separated structure using a solvent that swells the minor block, but does not swell the major, framework block. Collapse of the swollen polymer during solvent removal can produce pores in the minor phase.^[10]

BCP Removal. A reactive additive that is preferentially located in one of the blocks is polymerized and/or crosslinked and the original structure-defining BCP is then removed (illustrated schematically in Figure 2c). This approach can be used to generate porous ceramics and porous carbons that are templated by the BCP microphase-separated structure. Block copolymer macromolecular structural chemistry is first used to generate a microphase-separated structure, and then, synthesis chemistry is used to generate the desired wall material.

6. Emulsion Templating: Space – the Porous Frontier

Emulsion templating (illustrated schematically in Figure 3a) was originally associated with hydrophobic, crosslinked, porous polymer monoliths known as “polyHIPEs” (PHs). PHs were originally synthesized using free radical polymerization in the external phases of water-in-oil (w/o) high internal phase emulsions (HIPEs), emulsions containing internal phase contents greater than 74% (the maximum packing fraction of monodisperse, undeformable spheres).^[54] The emulsion’s two-phase structure thus serves as a template for generating a porous polymer monolith. Removing the internal phase droplets (typically tens of micrometres in diameter) leaves

voids that are highly interconnected through multiple holes (typically micrometres in diameter) in the polymer walls. The synthesis of hydrogel PHs (HG-PHs) within oil-in-water (o/w) HIPEs and the synthesis of a wide variety of polymers within a wide variety of HIPEs have extended the applicability of emulsion templating even further.^[55–56] PHs have been applied as flow-through supports, membranes, and column packing, as adsorbents-absorbents (for removing organic and metal ion contaminants from water and for oil-spill clean-up), as scaffolds for tissue engineering, as containers for controlled release, and as precursors for porous inorganics and porous carbons. They have been applied as monoliths, as membranes, as beads, as injectable HIPEs for biomedical applications, and as inks for additive manufacturing.^[57–59]

Polymers with hierarchically porous structures have critical applicative advantages since they combine high specific surface areas, ease of micropore accessibility, and fast transport pathways. Emulsion-templating offers a highly versatile spectrum of porous polymer possibilities and serves, in some ways, as a microcosm of the various issues involved in the chemistry of porous polymers.^[60–70] Many of the polymerization chemistries used in the other porous polymer systems mentioned above can be applied within emulsion-templated systems. In addition, many of the other pore generation processes mentioned above (hypercrosslinking, self-assembly, phase separation, sol-gel formation, and foaming) can be applied within emulsion-templated systems to generate hierarchical porosities with advantageous applicability.

6.1 Polymerization: And They Shall Become One

Conventional free radical polymerization (FRP) is, by far, the polymerization chemistry most commonly used for PH synthesis. Recently, a variety of controlled radical polymerizations (e.g. atom transfer radical polymerization), ring opening polymerizations, and SGPs have been developed for PH synthesis, with non-aqueous oil-in-oil (o/o) emulsions used for water-sensitive polymerizations.^[61,70] The adoption of new polymerization chemistries for emulsion templating not only impacts the macromolecular structures available, but also the pore-generation processes. In the generation of porous polymers there are often multiple processes, such as phase separation and/or gas expansion, that occur simultaneously with polymerization. For the successful generation of porous polymers, the relative progress of the different processes must be synchronized. In emulsion templating, polymerization and emulsion destabilization can occur simultaneously, especially for polymerizations at higher temperatures. Advances in polymerization chemistry have enabled syntheses at lower temperatures (e.g., redox systems, UV initiation) and advances in designing macromolecular structures have enabled *locking-in* the emulsion-templated structure before extensive emulsion destabilization can occur.

Emulsion templating offers advantageous options in polymerization reactions that are not available in single-phase

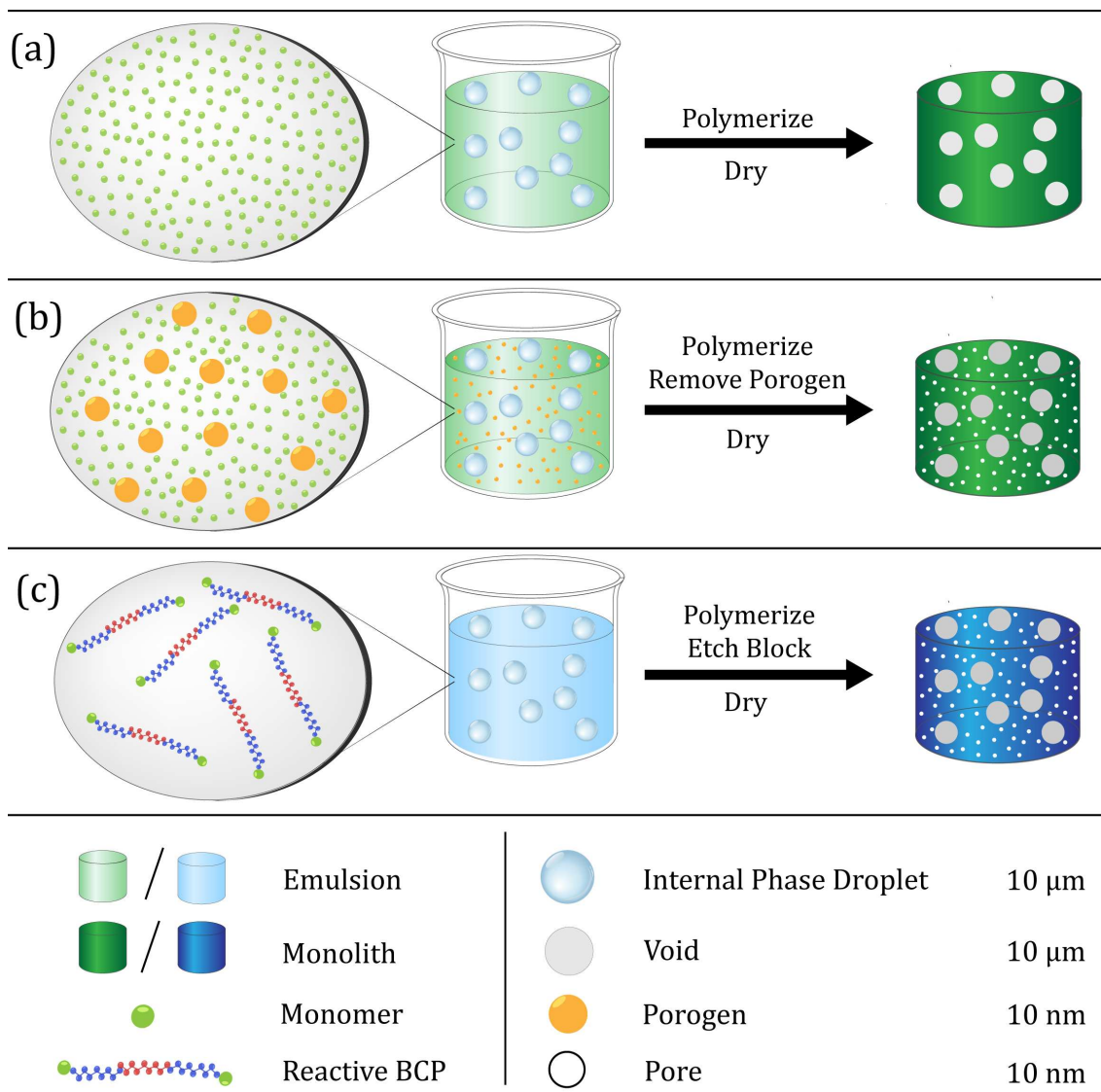


Figure 3. A schematic illustration describing emulsion templating when the external phase contains: (a) monomers only, for a macroporous structure; (b) monomers and a phase-separating porogenic component (solvent, degradable polymer) for a hierarchical porosity that includes sub-micrometre pores; (c) self-assembling BCPs with a degradable block for a hierarchical porosity that includes mesoporosity.

polymerizations of the same monomers, including interfacial FRP initiation (the initiator is in the internal phase) and interfacial SGP (one of the monomers is in the external phase and the other is in the internal phase). Interestingly, polymerization chemistries that involve the HIPE interface can also be used to produce truly closed-cell structures instead of the highly interconnected open-cell structures that are typical of emulsion templating.^[71]

6.2 Emulsification: Divide the Waters from the Waters

Robust emulsion stabilization chemistries are vital for the successful synthesis of emulsion-templated porous polymers.

Originally, only relatively large amounts of a limited number of surfactants were able to stabilize HIPEs. These surfactants proved effective at reducing the size of the internal phase droplets, but could leach out during use. Recently, a variety of BCP surfactants were used to promote anchoring the surfactant in the polymer wall through entanglement. These BCPs can be used to tune the surface chemistry by designing a specific block that would spontaneously migrate to the oil-water interface.^[72–75] Most recently, surfactants with polymerizable groups were covalently anchored to the polymer wall surface, and in some syntheses, the polymerizable surfactant was the only monomer.^[76–84] Pickering HIPEs, HIPEs stabilized using either inorganic or polymeric amphiphilic nanoparticles (NPs), have also been developed. One advantage of Pickering HIPEs

is the relatively high stabilization efficiencies exhibited at relatively low NP concentrations.^[66,85–90] Stabilizing NPs that are functionalized can also play critical roles in the polymerization reaction (the NPs can bear initiation sites) and in defining the macromolecular structure (the NPs can bear crosslinking sites). The presence of an internal phase and the use of a stabilization system thus provide additional factors that can be used to enable the generation of novel porous polymer systems.

6.3 Polymer Wall Structure: Behold, There Was a Hole in the Wall

The continually expanding list of polymers used successfully in the generation of emulsion-templated porous polymers follows the innovative developments in the chemistry of polymerization and in the chemistry of emulsion stabilization. The earliest PHs were hydrophobic, amorphous polymers (styrenics and (meth)acrylates). Emulsion templating has now been extensively extended through the development of HG-PHs, semi-crystalline PHs, organic-inorganic hybrid PHs, interpenetrating polymer network PHs, cyclic polymer PHs, and SGP PHs.^[91–97] The hypercrosslinking, self-assembly, phase separation, sol-gel formation, and foaming processes that have been used to produce the wide variety of porous polymer systems available can also be applied within the walls of emulsion-templated polymers to produce additional scales of porous structure (schematically illustrated in Figures 3b and c).

Post-synthesis hypercrosslinking of styrenic PHs via Friedel-Crafts reactions has been used to achieve PHs with specific surface areas as high as 1600 m²/g.^[62,98–103] BCP self-assembly, with semi-crystalline endblock domains and micro-phase-separated midblock domains, has been observed within the walls of a PH based on a methacrylated triblock copolymer as the only monomer.^[104] Phase separation during polymerization and/or crosslinking was observed within HIPEs containing a significant amount of solvent in the external phase, achieving specific surface areas as high as 570 m²/g.^[93,105–106] The incorporation of other pore-generating processes within the PH walls includes the generation of highly porous PH walls using gel formation and drying and the generation of foamed PH walls using CO₂-generating urea reactions.^[107–113] The application of the previously described routes used to generate microporosity and mesoporosity could also be applied within the PH walls to generate monoliths with hierarchical porosities. The potential inherent within designable wall chemistries can be used to exploit emulsion templating even further. For example, the development of chiral walls could enable the generation of PHs for advanced separation processes and the development of supramolecular walls with reversible associations could enable the generation of self-healing PHs.

Emulsion templating has not been limited to polymers, with the emulsion-templated polymers themselves acting as

templates for the generation of porous inorganics and porous carbons. Porous inorganics (silica, titania, zirconia, alumina) have been generated through the calcination of organic-inorganic hybrid PHs or nanocomposite PHs.^[114] Porous carbons have been generated through carbonization of PHs based on acrylonitrile, styrenics, polyphenols, furfuryl alcohol, and resorcinol-formaldehyde.^[70]

6.4 Environmental Impact: From Dust to Dust

One issue of paramount societal importance is the environmental impact of polymers. Polymerization chemistries are being developed to take advantage of monomers from renewable resources and macromolecular structural chemistries are being developed to enhance degradability. PHs that were based on renewable resource monomers such as polyphenols (e.g., tannin, tannic acid, lignin), plant oils (e.g., soybean, castor), polysaccharides (e.g., alginate, chitosan, dextrin, pectin), and lactide have recently been developed,^[62,115–120] as were PHs that were based on polymers containing degradable groups (e.g., esters).^[57–60,62,121–129] In addition, the recent advent of reactive surfactants and/or reactive nanoparticles for HIPE stabilization has produced a significant reduction in the amounts of leachable components.

7. Outlook: The Shape of Pores to Come

The development of novel and innovative porous polymers often tracks the development of novel and innovative polymerization chemistries and macromolecular structural chemistries. The key to producing porous polymers can lie in achieving a balance in the often simultaneous processes of generating the pores and *locking-in* the porous structure. Much of the current porous polymer research and development is focused upon applications with significant societal and environmental implications.

7.1 Applications: Earth, Water, Air, and Fire

Health. Porous polymer dialysis membranes are essential for blood purification. Intensive efforts are now being expended for the development of porous polymers for controlled release and tissue engineering applications. **Water.** Porous polymer membranes are an integral part of the reverse osmosis process used for generating drinkable water. Presently, there is also a great deal of work that is focused on the development of porous polymers both for the removal of organic and metal ion contaminants from water and for oil-spill clean-up. **Air.** Porous polymer membranes are central components of the gas separation processes used for gas purification and recovery and are also being developed for CO₂ capture applications. **Energy.** Reducing the consumption of fossil fuels and developing alternative energy sources are both environmental

priorities. In transportation, whether automotive or aerospace, reducing the vehicle mass will produce significant reductions in fuel consumption. Polymers have always been at the forefront of these efforts, whether as plastics, as polymer composites, or as lightweight polymer foams. Porous polymers are also playing important roles in advanced energy applications: in the development of lithium-polymer storage batteries (e.g., nanoporous separators,^[130] porous solid polymer electrolytes^[131]), in the development of polymer electrolyte membrane fuel cells (PEMFCs),^[132–133] and in the development of hydrogen storage systems.^[15,99,134–137]

Acknowledgements

I thank the Editors for their invitation to participate in this discussion on *The Chemistry of Polymers*. The partial support of the Israel Science Foundation (519/16), the Israel Ministry of Science (880011), and the United States – Israel Binational Science Foundation (2016630 and 2018099) is gratefully acknowledged.

References

- [1] H. Staudinger, *Berichte der deutschen chemischen Gesellschaft (A and B Series)* **1920**, *53*, 1073–1085.
- [2] W. H. Chapman, D. W. Pounder, E. A. Murphy, E. W. B. Owen, *BP 332,525*, Dunlop Rubber Co, Ltd, Great Britain **1929**.
- [3] E. A. Murphy, E. W. B. Owen, *US1929603 A*, Dunlop Rubber Co, Ltd, United States **1933**.
- [4] E. W. Madge, *Latex Foam Rubber*, MacLaren & Sons, Ltd, London **1962**.
- [5] S.-T. Lee, C. B. Park, N. S. Ramesh, *Polymeric Foams: Science and Technology*, Taylor and Francis, Boca Raton FL **2007**.
- [6] H. Bechhold, *Zeitschrift für Physikalische Chemie* **1907**, *60 U*, 257–318.
- [7] S. L. Bigelow, A. Gemberlin, *J. Am. Chem. Soc.* **1907**, *29*, 1576–1589.
- [8] S. Loeb, S. Sourirajan, *Saline Water Conversion—II, Vol. 38*, American Chemical Society **1963**, pp. 117–132.
- [9] R. W. Baker, *Encyclopedia of Polymer Science and Technology*, John Wiley & Sons, Inc. **2002**.
- [10] D. Wu, F. Xu, B. Sun, R. Fu, H. He, K. Matyjaszewski, *Chem. Rev.* **2012**, *112*, 3959–4015.
- [11] M. T. Gokmen, F. E. Du Prez, *Prog. Polym. Sci.* **2012**, *37*, 365–405.
- [12] S. Qiu, T. Ben, *Porous Polymers: Design, Synthesis and Applications*, Royal Society of Chemistry, Cambridge, UK **2016**.
- [13] S. Krause, *Polymer Blends, Vol. 1* (Eds.: D. R. Paul, S. Newman), Academic Press, New York, NY **1978**, pp. 15–113.
- [14] N. B. McKeown, P. M. Budd, *Porous Polymers* (Eds.: M. S. Silverstein, N. R. Cameron, M. A. Hillmyer), Wiley, New York, NY **2011**, pp. 3–29.
- [15] R. Dawson, A. I. Cooper, D. J. Adams, *Prog. Polym. Sci.* **2012**, *37*, 530–563.
- [16] E. M. Todd, M. A. Hillmyer, *Porous Polymers* (Eds.: M. S. Silverstein, N. R. Cameron, M. A. Hillmyer), John Wiley & Sons, New York, NY **2011**, pp. 31–78.
- [17] L. Qian, H. Zhang, *Porous Polymers* (Eds.: M. S. Silverstein, N. R. Cameron, M. A. Hillmyer), John Wiley & Sons, New York, NY **2011**, pp. 79–117.
- [18] H. Staudinger, W. Heuer, *Berichte der deutschen chemischen Gesellschaft (A and B Series)* **1934**, *67*, 1164–1172.
- [19] R. B. Merrifield, *J. Am. Chem. Soc.* **1963**, *85*, 2149–2154.
- [20] V. Davankov, S. Rogozhin, M. Tsyurupa, *Mezhdunarodnaya Kniga* **1973**, *15*, 463–465.
- [21] J. Huang, S. R. Turner, *Polym. Rev.* **2018**, *58*, 1–41.
- [22] O. M. Yaghi, G. Li, H. Li, *Nature* **1995**, *378*, 703–706.
- [23] H. Li, M. Eddaoudi, M. O’Keeffe, O. M. Yaghi, *Nature* **1999**, *402*, 276–279.
- [24] J.-X. Jiang, A. Cooper, *Top. Curr. Chem.* **2010**, *293*, 1–33.
- [25] A. G. Slater, A. I. Cooper, *Science* **2015**, *348*, aaa8075.
- [26] T. Hasell, A. I. Cooper, *Nat. Rev. Mater.* **2016**, *1*, 16053.
- [27] A. P. Côté, A. I. Benin, N. W. Ockwig, M. O’Keeffe, A. J. Matzger, O. M. Yaghi, *Science* **2005**, *310*, 1166–1170.
- [28] A. I. Cooper, *Adv. Mater.* **2009**, *21*, 1291–1295.
- [29] P. Kuhn, M. Antonietti, A. Thomas, *Angew. Chem. Int. Ed.* **2008**, *47*, 3450–3453; *Angew. Chem.* **2008**, *120*, 3499–3502.
- [30] T. Ben, H. Ren, S. Ma, D. Cao, J. Lan, X. Jing, W. Wang, J. Xu, F. Deng, J. M. Simmons, S. Qiu, G. Zhu, *Angew. Chem. Int. Ed.* **2009**, *48*, 9457–9460; *Angew. Chem.* **2009**, *121*, 9621–9624.
- [31] P. M. Budd, E. S. Elabas, B. S. Ghanem, S. Makhseed, N. B. McKeown, K. J. Msayib, C. E. Tattershall, D. Wang, *Adv. Mater.* **2004**, *16*, 456–459.
- [32] C. R. DeBlase, W. R. Dichtel, *Macromolecules* **2016**, *49*, 5297–5305.
- [33] M. W. Matsen, F. S. Bates, *Macromolecules* **1996**, *29*, 1091–1098.
- [34] M. W. Matsen, F. S. Bates, *J. Chem. Phys.* **1997**, *106*, 2436–2448.
- [35] C. M. Bates, F. S. Bates, *Macromolecules* **2017**, *50*, 3–22.
- [36] G. Liu, J. Ding, S. Stewart, *Angew. Chem. Int. Ed.* **1999**, *38*, 835–838; *Angew. Chem.* **1999**, *111*, 884–887.
- [37] B. d Boer, U. Stalmach, H. Nijland, G. Hadziioannou, *Adv. Mater.* **2000**, *12*, 1581–1583.
- [38] T. P. Russell, T. Thurn-Albrecht, M. Tuominen, E. Huang, C. J. Hawker, *Macromol. Symp.* **2000**, *159*, 77–88.
- [39] M. A. Hillmyer, *Adv. Polym. Sci.* **2005**, *190*, 137–181.
- [40] J. Bang, S. H. Kim, E. Drockenmuller, M. J. Misner, T. P. Russell, C. J. Hawker, *J. Am. Chem. Soc.* **2006**, *128*, 7622–7629.
- [41] S. P. Nunes, *Macromolecules* **2016**, *49*, 2905–2916.
- [42] C. Sinturel, M. Vayer, M. Morris, M. A. Hillmyer, *Macromolecules* **2013**, *46*, 5399–5415.
- [43] G. J. d A A Soler-Illia, E. L. Crepaldi, D. Grosso, C. Sanchez, *Curr. Opin. Colloid Interface Sci.* **2003**, *8*, 109–126.
- [44] J. Lee, J. Kim, Y. Lee, S. Yoon, S. M. Oh, T. Hyeon, *Chem. Mater.* **2004**, *16*, 3323–3330.
- [45] F. Zhang, Y. Meng, D. Gu, Yan, Z. Chen, B. Tu, D. Zhao, *Chem. Mater.* **2006**, *18*, 5279–5288.
- [46] S. C. Warren, L. C. Messina, L. S. Slaughter, M. Kamperman, Q. Zhou, S. M. Gruner, F. J. DiSalvo, U. Wiesner, *Science* **2008**, *320*, 1748–1752.
- [47] J. P. McGann, M. Zhong, E. K. Kim, S. Natesakhawat, M. Jaroniec, J. F. Whitacre, K. Matyjaszewski, T. Kowalewski, *Macromol. Chem. Phys.* **2012**, *213*, 1078–1090.
- [48] J. G. Werner, T. N. Hoheisel, U. Wiesner, *ACS Nano* **2013**, *8*, 731–743.

- [49] R. Yuan, M. Kopeć, G. Xie, E. Gottlieb, J. W. Mohin, Z. Wang, M. Lamson, T. Kowalewski, K. Matyjaszewski, *Polymer* **2017**, *126*, 352–359.
- [50] T.-C. Lin, K.-C. Yang, P. Georgopoulos, A. Avgeropoulos, R.-M. Ho, *Polymer* **2017**, *126*, 360–367.
- [51] M. Kopeć, M. Lamson, R. Yuan, C. Tang, M. Kruk, M. Zhong, K. Matyjaszewski, T. Kowalewski, *Prog. Polym. Sci.* **2019**, *92*, 89–134.
- [52] K. Shin, K. A. Leach, J. T. Goldbach, D. H. Kim, J. Y. Jho, M. Tuominen, C. J. Hawker, T. P. Russell, *Nano Lett.* **2002**, *2*, 933–936.
- [53] X.-B. Wang, T.-Y. Lo, H.-Y. Hsueh, R.-M. Ho, *Macromolecules* **2013**, *46*, 2997–3004.
- [54] N. R. Cameron, D. C. Sherrington, *Adv. Polym. Sci.* **1996**, *126*, 163–214.
- [55] N. Cohen, M. S. Silverstein, *Macromolecules* **2012**, *45*, 1612–1621.
- [56] M. Ovidia, M. S. Silverstein, *Polym. Int.* **2016**, *65*, 280–289.
- [57] J. L. Robinson, R. S. Moglia, M. C. Stuebben, M. A. P. McEnery, E. Cosgriff-Hernandez, *Tissue Eng.* **2013**, *20*, 1103–1112.
- [58] R. S. Moglia, J. L. Holm, N. A. Sears, C. J. Wilson, D. M. Harrison, E. Cosgriff-Hernandez, *Biomacromolecules* **2011**, *12*, 3621–3628.
- [59] J. L. Robinson, M. A. P. McEnery, H. Pearce, M. E. Whitely, D. J. Munoz-Pinto, M. S. Hahn, H. Li, N. A. Sears, E. Cosgriff-Hernandez, *Tissue Eng.* **2016**, *22*, 403–414.
- [60] M. S. Silverstein, *Polymer* **2014**, *55*, 304–320.
- [61] M. S. Silverstein, *Prog. Polym. Sci.* **2014**, *39*, 199–234.
- [62] M. S. Silverstein, *Polymer* **2017**, *126*, 261–282.
- [63] N. R. Cameron, *Polymer* **2005**, *46*, 1439–1449.
- [64] H. Zhang, A. I. Cooper, *Soft Matter* **2005**, *1*, 107–113.
- [65] E. Ruckenstein, *Adv. Polym. Sci.* **1997**, *127*, 1–58.
- [66] N. Brun, S. Ungureanu, H. Deleuze, R. Backov, *Chem. Soc. Rev.* **2011**, *40*, 771–788.
- [67] S. D. Kimmins, N. R. Cameron, *Adv. Funct. Mater.* **2011**, *21*, 211–225.
- [68] I. Pulko, P. Krajnc, *Encyclopedia of Polymer Science and Technology*, John Wiley & Sons, Inc. **2017**.
- [69] I. Pulko, P. Krajnc, *Macromol. Rapid Commun.* **2012**, *33*, 1731–1746.
- [70] T. Zhang, R. A. Sanguramath, S. Israel, M. S. Silverstein, *Macromolecules* **2019**, *52*, 5445–5479.
- [71] I. Gurevitch, M. S. Silverstein, *Macromolecules* **2012**, *45*, 6450–6456.
- [72] S. Kovačić, M. S. Silverstein, *Macromol. Rapid Commun.* **2016**, *37*, 1814–1819.
- [73] T. Zhang, Z. Xu, Y. Wu, Q. Guo, *Ind. Eng. Chem. Res.* **2016**, *55*, 4499–4505.
- [74] T. Zhang, Z. Xu, Z. Cai, Q. Guo, *Phys. Chem. Chem. Phys.* **2015**, *17*, 16033–16039.
- [75] P. Viswanathan, D. W. Johnson, C. Hurley, N. R. Cameron, G. Battaglia, *Macromolecules* **2014**, *47*, 7091–7098.
- [76] S. Kovačić, F. Preishuber-Pflügl, D. Pahovnik, E. Žagar, C. Slugovc, *Chem. Commun.* **2015**, *51*, 7725–7728.
- [77] K. Mathieu, C. Jérôme, A. Debuigne, *Macromolecules* **2015**, *48*, 6489–6498.
- [78] A. Khodabandeh, R. Dario Arrua, C. T. Desire, T. Rodemann, S. A. F. Bon, S. C. Thickett, E. F. Hilder, *Polym. Chem.* **2016**, *7*, 1803–1812.
- [79] K. Mathieu, J. De Winter, C. Jérôme, A. Debuigne, *Polym. Chem.* **2017**, *8*, 1850–1861.
- [80] T. Zhang, M. S. Silverstein, *Macromolecules* **2018**, *51*, 3828–3835.
- [81] T. Zhang, M. S. Silverstein, *Polymer* **2019**, *168*, 146–154.
- [82] Z. Li, T. Ming, J. Wang, T. Ngai, *Angew. Chem. Int. Ed.* **2009**, *48*, 8490–8493; *Angew. Chem.* **2009**, *121*, 8642–8645.
- [83] Y. Zhu, R. Zhang, S. Zhang, Y. Chu, J. Chen, *Langmuir* **2016**, *32*, 6083–6088.
- [84] Z. Li, M. Xiao, J. Wang, T. Ngai, *Macromol. Rapid Commun.* **2013**, *34*, 169–174.
- [85] I. Gurevitch, M. S. Silverstein, *Macromolecules* **2011**, *44*, 3398–3409.
- [86] P. J. Colver, S. A. F. Bon, *Chem. Mater.* **2007**, *19*, 1537–1539.
- [87] A. Menner, V. Ikem, M. Salgueiro, M. S. P. Shaffer, A. Bismarck, *Chem. Commun.* **2007**, 4274–4276.
- [88] M. C. Hermant, B. Klumperman, C. E. Koning, *Chem. Commun.* **2009**, 2738–2740.
- [89] I. Gurevitch, M. S. Silverstein, *J. Polym. Sci. Part A* **2010**, *48*, 1516–1525.
- [90] V. O. Ikem, A. Menner, A. Bismarck, *Langmuir* **2010**, *26*, 8836–8841.
- [91] H. Tai, A. Sergienko, M. S. Silverstein, *Polym. Eng. Sci.* **2001**, *41*, 1540–1552.
- [92] H. Tai, A. Sergienko, M. S. Silverstein, *Polymer* **2001**, *42*, 4473–4482.
- [93] O. Kulygin, M. S. Silverstein, *Soft Matter* **2007**, *3*, 1525–1529.
- [94] I. Gurevitch, M. S. Silverstein, *Soft Matter* **2012**, *8*, 10378–10387.
- [95] J. Normatov, M. S. Silverstein, *J. Polym. Sci. Part A* **2008**, *46*, 2357–2366.
- [96] J. Normatov, M. S. Silverstein, *Chem. Mater.* **2008**, *20*, 1571–1577.
- [97] S. Livshin, M. S. Silverstein, *Soft Matter* **2008**, *4*, 1630–1638.
- [98] S. Israel, I. Gurevitch, M. S. Silverstein, *Polymer* **2015**, *72*, 453–463.
- [99] M. G. Schwab, I. Senkovska, M. Rose, N. Klein, M. Koch, J. Pahnke, G. Jonschker, B. Schmitz, M. Hirscher, S. Kaskel, *Soft Matter* **2009**, *5*, 1055–1059.
- [100] U. Sevsšek, J. Brus, K. Jeřábek, P. Krajnc, *Polymer* **2014**, *55*, 410–415.
- [101] F. Yi, Y. Gao, H. Li, L. Yi, D. Chen, S. Lu, *Electrochim. Acta* **2016**, *211*, 768–776.
- [102] R. T. Woodward, A. Jobbe-Duval, S. Marchesini, D. B. Anthony, C. Petit, A. Bismarck, *Polymer* **2017**, *115*, 146–153.
- [103] S. Mezhoud, M. Paljevac, A. Koler, B. Le Droumaguet, D. Grande, P. Krajnc, *React. Funct. Polym.* **2018**, *132*, 51–59.
- [104] T. Zhang, M. S. Silverstein, *Macromolecules* **2018**, *51*, 3828–3835.
- [105] P. Pakeyangkoon, R. Magaraphan, P. Malakul, M. Nithitanakul, *Macromol. Symp.* **2008**, *264*, 149–156.
- [106] M. S. Silverstein, H. W. Tai, A. Sergienko, Y. L. Lumelsky, S. Pavlovsky, *Polymer* **2005**, *46*, 6682–6694.
- [107] B. H. L. Oh, A. Bismarck, M. B. Chan-Park, *Macromol. Rapid Commun.* **2015**, *36*, 364–372.
- [108] Y. Hu, W. Han, Y. Chen, R. Zou, Y. Ouyang, W. Zhou, Z. Yang, C. Wang, *Macromol. Mater. Eng.* **2017**, *302*, 1600367.
- [109] D. B. Mahadik, H.-N.-R. Jung, W. Han, H. H. Cho, H.-H. Park, *Compos. Sci. Technol.* **2017**, *147*, 45–51.
- [110] T. Zhang, Y. Wu, Z. Xu, Q. Guo, *Chem. Commun.* **2014**, *50*, 13821–13824.
- [111] Y. Wu, T. Zhang, Z. Xu, Q. Guo, *J. Mater. Chem. A* **2015**, *3*, 1906–1909.
- [112] T. Zhang, G. Xu, Z.-F. Li, O. Regev, M. Maddumaarachchi, F. D. Blum, *J. Colloid Interface Sci.* **2015**, *451*, 161–169.
- [113] T. Zhang, Q. Guo, *Chem. Commun.* **2016**, *52*, 4561–4564.
- [114] H. Zhang, G. C. Hardy, Y. Z. Khimiyak, M. J. Rosseinsky, A. I. Cooper, *Chem. Mater.* **2004**, *16*, 4245–4256.

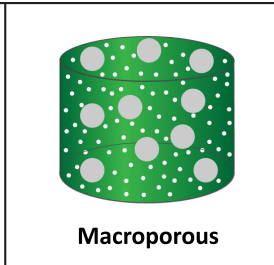
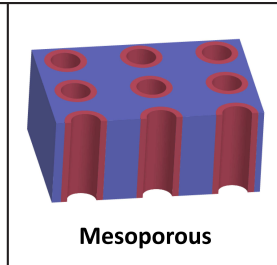
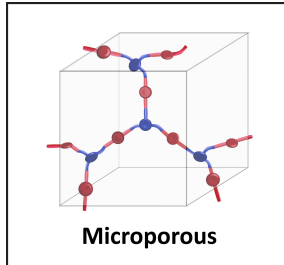
- [115] A. Szczurek, V. Fierro, M. Thébault, A. Pizzi, A. Celzard, *Eur. Polym. J.* **2016**, *78*, 195–212.
- [116] A. Szczurek, A. Martínez de Yuso, V. Fierro, A. Pizzi, A. Celzard, *Mater. Des.* **2015**, *79*, 115–126.
- [117] A. Foulet, M. Birot, R. Backov, G. Sonnemann, H. Deleuze, *Mater. Today Commun.* **2016**, *7*, 108–116.
- [118] A. Foulet, M. Birot, G. Sonnemann, H. Deleuze, *React. Funct. Polym.* **2015**, *90*, 15–20.
- [119] C. Forgacz, M. Birot, H. Deleuze, *J. Appl. Polym. Sci.* **2015**, *132*, 41215.
- [120] L. Weinstock, R. A. Sanguramath, M. S. Silverstein, *Polym. Chem.* **2019**, *10*, 1498–1507.
- [121] M. G. Pérez-García, M. C. Gutiérrez, J. D. Mota-Morales, G. Luna-Bárceñas, F. del Monte, *ACS Appl. Mater. Interfaces* **2016**, *8*, 16939–16949.
- [122] D. W. Johnson, C. R. Langford, M. P. Didsbury, B. Lipp, S. A. Przyborski, N. R. Cameron, *Polym. Chem.* **2015**, *6*, 7256–7263.
- [123] Y. Hu, H. Gao, Z. Du, Y. Liu, Y. Yang, C. Wang, *J. Mater. Chem. B* **2015**, *3*, 3848–3857.
- [124] M. Lamson, Y. Epshtein-Assor, M. S. Silverstein, K. Matyjaszewski, *Polymer* **2013**, *54*, 4480–4485.
- [125] S. Caldwell, D. W. Johnson, M. P. Didsbury, B. A. Murray, J. J. Wu, S. A. Przyborski, N. R. Cameron, *Soft Matter* **2012**, *8*, 10344–10351.
- [126] Y. Lumelsky, J. Zoldan, S. Levenberg, M. S. Silverstein, *Macromolecules* **2008**, *41*, 1469–1474.
- [127] D. David, M. S. Silverstein, *J. Polym. Sci. Part A* **2009**, *47*, 5806–5814.
- [128] Y. Lumelsky, I. Lalush-Michael, S. Levenberg, M. S. Silverstein, *J. Polym. Sci. Part A* **2009**, *47*, 7043–7053.
- [129] Y. Lumelsky, M. S. Silverstein, *Macromolecules* **2009**, *42*, 1627–1633.
- [130] J. L. Weininger, F. F. Holub, *J. Electrochem. Soc.* **1970**, *117*, 340–342.
- [131] K. Murata, S. Izuchi, Y. Yoshihisa, *Electrochim. Acta* **2000**, *45*, 1501–1508.
- [132] K. A. Mauritz, R. B. Moore, *Chem. Rev.* **2004**, *104*, 4535–4586.
- [133] R. Gloukhovski, V. Freger, Y. Tsur, *Rev. Chem. Eng.* **2018**, *34*, 455–479.
- [134] N. B. McKeown, P. M. Budd, D. Book, *Macromol. Rapid Commun.* **2007**, *28*, 995–1002.
- [135] F. Su, C. L. Bray, B. Tan, A. I. Cooper, *Adv. Mater.* **2008**, *20*, 2663–2666.
- [136] J. Weber, M. Antonietti, A. Thomas, *Macromolecules* **2008**, *41*, 2880–2885.
- [137] Q. Chen, M. Luo, P. Hammershøj, D. Zhou, Y. Han, B. W. Laursen, C.-G. Yan, B.-H. Han, *J. Am. Chem. Soc.* **2012**, *134*, 6084–6087.

Manuscript received: January 7, 2020

Revised manuscript received: February 9, 2020

Version of record online: ■■, ■■

ESSAYS



M. S. Silverstein

1 – 12

**The Chemistry of Porous
Polymers: The Holy Grail**
