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Emulsion-templated polymers: Contemporary contemplations

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A B S T R A C T

Emulsion-templated porous polymers (polyHIPEs) with highly interconnected voids that range from a few micrometers to hundreds of micrometers are typically synthesized within the external phases of high internal phase emulsions (HIPEs), emulsions containing more than 74% internal phase. Recent advances in emulsion-templated polymers include new developments in HIPE formation, polymerization chemistries, macromolecular structures, crosslinking strategies, porous architectures, and surface functionalization. This article focuses upon emulsion-templated polymers through the prism of the research and development work in our laboratory. The innovative emulsion-templated systems described include shape-memory polymers, encapsulation systems, hydrogels, and porous carbons. This article also briefly reviews recent work in the field and draws some conclusions regarding trends and future directions. The abundance of diverse and disparate research directions pursued under the banner of "emulsion templating" is indicative of its high degree of versatility. Novel families of porous polymers with unique properties can now be devised and designed through the advances described herein.

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1. Introduction

1.1. Porous polymers

The advantages of polymers include the infinite variability of available macromolecular structures and the ease of processability. Porous polymers leverage these advantages to generate monoliths, films, and beads, often with well-defined porosities and high specific surface areas [1-4]. The high level of interest in the research and development of porous polymer systems is a recent phenomenon, as seen in Fig. 1 (the left-hand *y*-axis shows the results of a relatively restrictive literature search for articles that contain both “porous” and “polymer”). Until 1990, there were only a few tens of articles per year that fulfilled the “porous” and “polymer” criterion. In 1991, the number of articles “jumped” to several hundreds and has increased exponentially since then, with 3400 + articles in 2016. The dashed line in Fig. 1 represents the *y*-axis maximum in the corresponding graph from a previous literature search (the 2200 + articles published in 2012) [5].

The increase in the number of “porous” + “polymer” articles published from 2012 is remarkable. The articles published in the last 4 years, 2013 to 2016, account for 38% of all the articles that have been published. This recent surge in porous polymer research and development reflects the added-value anticipated for the numerous applications, high-tech and low-tech, that include: absorbents and adsorbents; biomedical devices; membranes, supports, and packing; lightweight foams; microelectronics and optics; responsive/smart materials; and precursors for porous ceramics and porous carbons. This article will use the International Union of Pure and Applied Chemistry classifications for porosity: microporous (less than 2 nm), mesoporous (between 2 and 50 nm), and macroporous (greater than 50 nm).

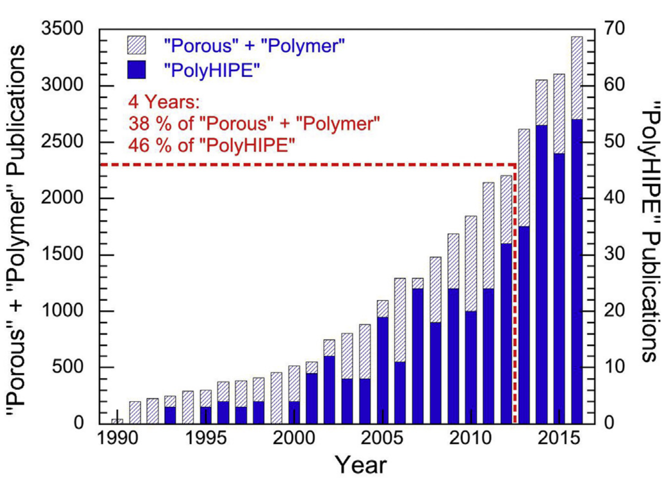

Figure 1. The number of publications per year (1989–2016) resulting from a search for: (left-hand *y-axis*) both “porous” and “polymer”; (right-hand *y-axis*) “polyHIPE”. The dashed line indicates the *y-axis* maximum in the corresponding graph from 2012.

The approaches to generating porous polymers include: macromolecular design of porous frameworks or rigid structures with inherent microporosity; porogen incorporation and phase inversion; and templating. There are several templating methods that can be used to produce porous polymers [6,7]: block copolymer templating, solid particle templating, and emulsion templating. Porous polymers templated within high internal phase emulsions are often termed “polyHIPEs”. The recent surge in publications on polyHIPEs (PHs) mirrors that for “porous” + “polymer”, as seen in Fig. 1 (the right-hand *y*-axis shows the results of a relatively restrictive literature search for articles that contain “polyHIPE”). The increase in the number of “polyHIPE” articles published from 2012 onward is even more remarkable than for “porous” + “polymer”, 46% of all the “polyHIPE” articles were published in the last 4 years (2013–2016). This article reviews recent emulsion-templating research and development work in the Macromolecular Materials Laboratory, Department of Materials Science and Engineering, Technion – Israel Institute of Technology.

1.2. Emulsion templating

A PH is typically synthesized through polymerization within the external phase (EP) of a HIPE, an emulsion containing more than 74% internal phase (IP) dispersed as individual droplets [7-9]. The synthesis of a hydrophobic polymer with a cellular structure synthesized within a water-in-oil (w/o) HIPE was first described in 1962 [10,11] and similar systems were developed over the next decade [12-16]. The terms “HIPE” and “polyHIPE” first appeared in a 1982 patent [17,18] to describe emulsion-templated styrene-based polymers. The 74% IP limit on “HIPE” is based on the maximum packing fraction of monodisperse solid spheres. Others have suggested a limit of 64% IP based on the random close packing of monodisperse solid spheres [19]. Open-cell, interconnected, porous structures have also been obtained at significantly lower internal volume fractions since the formation of the interconnecting holes is dependent upon a large number of synthesis parameters. Often, “medium internal phase emulsion” (MIPE) is used to describe IP volume fractions of 30–74% and “low internal phase emulsion” (LIPE) is used to describe IP volume fractions of less than 30% [20].

Typically, the macroporous structures in PHs are generated through the removal of the internal phase, with air-filled “voids” taking the place of the evacuated droplets. The voids, whose diameters can range from a few micrometers to hundreds of micrometers, are highly interconnected through holes that are formed in the polymer walls. A variety of terms are used to describe the different facets of emulsion-templated polymers [21]. For simplicity, the terms “HIPE” and “polyHIPE” will be used here for all the emulsion-templated systems, the term “void” will be used to describe the pores generated by evacuating the IP droplets, and the term “interconnecting holes” will be used to describe the void-connecting holes in the PH walls.

Originally, emulsion templating was used to synthesize porous,