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PolyHIPEs: Recent advances in emulsion-templated porous polymers

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ABSTRACT

Porous polymers with well-defined porosities and high specific surface areas in the form of monoliths, films, and beads are being used in a wide range of applications (reaction supports, separation membranes, tissue engineering scaffolds, controlled release matrices, responsive and smart materials) and are being used as templates for porous ceramics and porous carbons. The surge in the research and development of porous polymer systems is a rather recent phenomenon. PolyHIPEs are porous emulsion-templated polymers synthesized within high internal phase emulsions (HIPEs). HIPEs are highly viscous, paste-like emulsions in which the major, "internal" phase, usually defined as constituting more than 74% of the volume, is dispersed within the continuous, minor, "external" phase. This review focuses upon the recent advances in polyHIPEs involving innovations in polymer chemistry, macromolecular structure, multiphase architecture, surface functionalization, and nanoparticle stabilization. The effects of these innovations upon the natures of the resulting polyHIPE-based materials (including bicontinuous polymers, nanocomposites, hybrids, porous ceramics, and porous carbons) and upon the applications involving polyHIPEs are discussed. The advances in polyHIPEs described in this review are now being used to generate new families of porous materials with novel porous architectures and unique properties.

Abbreviations: AA, acrylic acid; AAm, acrylamide; AGET, activators generated by electron transfer; AN, acrylonitrile; ATRP, atom transfer radical polymerization; BA, butyl acrylate; BDP, boron-dipyrromethene; BDP-S, BDP-styrene; CB, carbon black; CNT, carbon nanotubes; CTAB, cetyltrimethylammonium bromide; DCPD, dicyclopentadiene; DVB, divinylbenzene; EBP, elastin-based side-chain polymers; EGDMA, ethylene glycol dimethacrylate; EHA, 2-ethylhexyl acrylate; EOF, electroosmotic flow; FA, furfuryl alcohol; FRP, free radical polymerization; GMA, glycidyl methacrylate; GSH, glutathione; GST, glutathione S-transferase; *H*, applied field; HgPtMS, 3-mercaptopropyltrimethoxysilane; HIPE, high internal phase emulsion; HPLC, high performance (or pressure) liquid chromatography; IL, ionic liquid; IL/O, ionic-liquid-in-oil; LCST, lower critical solution temperature; LDE, liquid droplet elastomer; *M*, magnetization; MAA, methacrylic acid; MAP, 4-(N-methylamino)pyridine; MBAm, N,N-methylenebisacrylamide; MG63, a human osteoblast-like cell line; MMA, methyl methacrylate; NiPAAm, N-isopropylacrylamide; NP, nanoparticle; O/O, oil-in-oil; O/W, oil-in-water; O/W/O, oil-in-water-in-oil; PAA, poly(acrylic acid); PAN, polyacrylonitrile; PCL, polycaprolactone; PEG, poly(ethylene glycol); PEGDMA, poly(ethylene glycol) dimethacrylate; PEO, poly(ethylene oxide); PFA, poly(furfuryl alcohol); PGA, polyglutaraldehyde; PGMA, poly(glycidyl methacrylate); PGPR, polyglycerol polyricinoleate; PHEMA, poly(hydroxyethyl methacrylate); PLGA, poly(L-lactide-co-glycolide); PMMA, poly(methyl methacrylate); PNiPAAm, poly(N-isopropylacrylamide); PPO, poly(propylene oxide); PS, polystyrene; PtBA, poly(tert-butyl acrylate); PU, polyurethane; PUU, poly(urethane urea); PVBC, poly(4-vinylbenzyl chloride); RAFT, reversible addition-fragmentation chain transfer polymerization; ROMP, ring opening metathesis polymerization; S, styrene; SEM, scanning electron microscopy; SMO, sorbitan monooleate (Span 80); SMP, shape memory polymer; SS, styrene sulfonate; SSA, specific surface area; SWCNT, single wall CNT; tBA, tert-butyl acrylate; TEM, transmission electron microscopy; TEOS, tetraethoxyorthosilane; THF, tetrahydrofuran; T_{m}, melting point; UV, ultraviolet; VBA, 1-(azidomethyl)-4-vinylbenzene; VBC, 4-vinylbenzyl chloride; VT, 1-vinyl-1,2,4-triazole; W/O, water-in-oil; W/O/W, water-in-oil-in-water.

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1. Introduction

1.1. Porous polymers

Porous materials have been shown to be useful for a wide range of applications [1,2]. Porous polymers are a subset of porous materials that take advantage of the ease of processability associated with polymers to generate monoliths, films, and beads, often with well-defined porosities and high specific surface areas (SSAs). Porous polymers are of interest for such applications as microelectronics, biomedical devices, membrane processes, and catalysis as well as for precursors that can be used to synthesize porous ceramics or porous carbon. This paper, a review of recent (2009–2012) work in emulsion-templated porous polymers, will use the pore size classifications adopted by the International Union of Pure and Applied Chemistry: microporous (less than 2 nm), mesoporous (between 2 and 50 nm), and macroporous (greater than 50 nm).

The high level of interest in the research and development of porous polymer systems is a recent phenomenon, as seen in Fig. 1 (left-hand *y*-axis). Fig. 1 presents 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 this criterion. In 1991, the number of articles that fulfilled this criterion "jumped" to several hundreds. The number of articles per year that fit this criterion has increased rapidly over the last 20 years, with over 2200 articles in 2012. On one side of the pore size spectrum, there is increasing interest in glassy polymers with inherent microporosity [3]. On the other side of the pore size spectrum, there is increasing interest in macroporous polymers generated using phase separation techniques and in polymer foams with millimeter-size pores [4].

There are several templating methods that can be used for the production of porous polymers, including block copolymer templating and colloidal templating. The removal of one of the nanometer-scale phases in microphase separated block copolymers can be used to generate mesoporous polymers [5]. In a typical colloidal templating scenario, a biphasic system is generated and then the continuous phase (or, in the case of bicontinuous systems, one of the co-continuous phases) is polymerized [6]. The colloidal entities serve to create porosity in the final polymeric material and are removed following polymerization. Depending on the nature of the colloidal system employed (emulsions, microemulsions, solid particles, or breath figure droplets), the characteristic pore size can range from a few nanometers to hundreds of micrometers.

1.2. HIPEs and polyHIPEs

PolyHIPEs are porous emulsion-templated polymers synthesized within high internal phase emulsions (HIPEs)

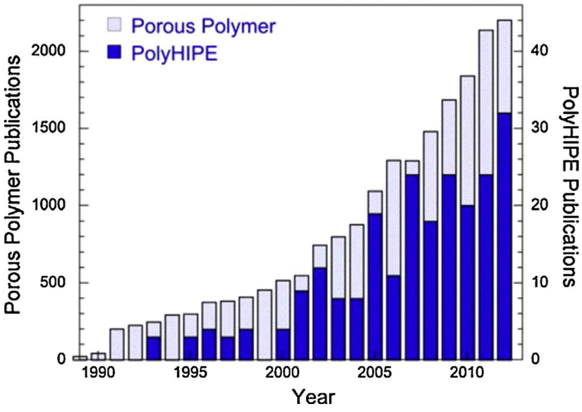

Fig. 1. The number of publications per year resulting from a topic search for: (left-hand *y*-axis) both "porous" and "polymer"; (right-hand *y*-axis) "polyHIPE".

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