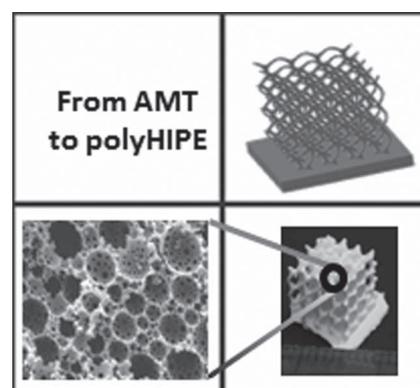


Hierarchically Porous Materials from Layer-by-Layer Photopolymerization of High Internal Phase Emulsions

Maja Sušec, Samuel Clark Ligon, Jürgen Stampfl,* Robert Liska, Peter Krajnc*

A combination of high internal phase emulsion (HIPE) templating and additive manufacturing technology (AMT) is applied for creating hierarchical porosity within an acrylate and acrylate/thiol-based polymer network. The photopolymerizable formulation is optimized to produce emulsions with a volume fraction of droplet phase greater than 80 vol%. Kinetic stability of the emulsions is sufficient enough to withstand in-mold curing or computer-controlled layer-by-layer stereolithography without phase separation. By including macroscale cellular cavities within the build file, a level of controlled porosity is created simultaneous to the formation of the porous microstructure of the polyHIPE. The hybrid HIPE–AMT technique thus provides hierarchically porous materials with mechanical properties tailored by the addition of thiol chain transfer agent.



1. Introduction

Materials with hierarchically structured pores can be applied in a wide array of fields such as catalysis^[1] and tissue engineering^[2,3] where defined pore size

distribution at different length scales is important. Colloidal templating is a popular approach for porous material preparation offering generally good control over pore size.^[4] More specifically, emulsions with a high volume fraction of droplet phase (high internal phase emulsions

M. Sušec

Centre of Excellence PoliMaT, Tehnološki park 24, 1000 Ljubljana, Slovenia; University of Maribor, Faculty of Chemistry and Chemical Engineering, PolyOrgLab, Smetanova 17, 2000 Maribor, Slovenia

Dr. S. C. Ligon

Vienna University of Technology, Institute of Applied Synthetic Chemistry, Getreidemarkt 9/163, 1060 Vienna, Austria

Prof. J. Stampfl

Vienna University of Technology, Institute of Materials Science and Technology, Favoritenstraße 9-11, 1060 Vienna, Austria

E-mail: juergen.stampfl@tuwien.ac.at

Prof. R. Liska

Vienna University of Technology, Institute of Applied Synthetic Chemistry, Getreidemarkt 9/163, 1060 Vienna, Austria

Prof. P. Krajnc

University of Maribor, Faculty of Chemistry and Chemical Engineering, PolyOrgLab, Smetanova 17, 2000 Maribor, Slovenia, Centre of Excellence PoliMaT, Tehnološki park 24, 1000 Ljubljana, Slovenia

E-mail: peter.krajnc@um.si

or HIPEs) can be used for the preparation of highly porous polymers with different levels of porosity.^[5,6] Within HIPE templating approach, there are already several examples of producing hierarchically porous monoliths^[7–9] or beads.^[10] While HIPE templating is quite flexible on micron and sub-micron length scales, it becomes increasingly difficult to produce material with a narrow pore size distribution once the droplets of emulsion exceed 50 μm in diameter.

To obtain a polymer from a HIPE (a polyHIPE), typically, monomers are included in the continuous phase and the droplet phase templates a first level of pores, which are interconnected via a series of a second (smaller) level of pores. Depending on the use of crosslinker and/or porogenic solvent, a third level of meso or micropores can be introduced within the polymer phase. The size of the droplets in a HIPE prior to polymerization largely governs the size of the first level of pores within a polyHIPE material. There are different factors influencing the droplet size in a HIPE, and methods for tuning include changing the energy input by mixing/shearing,^[11] adjusting temperature,^[12] adding solvents,^[12] aging of the emulsion,^[13] and changing surfactant composition and amount,^[14,15] to name but a few.

For creation of another level of pores it would be beneficial to apply the HIPE templating approach within a second parallel method, which allows construction of arbitrarily defined larger pores. Lithography-based additive manufacturing technologies (AMT) offer the possibility to selectively expose and harden photosensitive materials based on pre-defined computer aided design (CAD).^[16] Layer by layer assembly allows AMT methods to shape free standing complex three-dimensional parts with excellent feature resolution. Possible light sources, which are used in lithography-based AMT, include ultraviolet lasers in the case of stereolithography and digital mirror devices in the case of digital light processing (DLP).^[17]

Lithography-based AMT is primarily based on radical polymerization and almost all commercial resins are based on reactive (meth)acrylate monomers. To the best of the authors' knowledge, HIPEs have not yet been processed by lithography-based AMT methods. Indeed polyHIPE materials tend to be polymerized thermally with only a few examples published describing light-induced processes.^[18–20]

Therefore, the aim of this work was to provide a photopolymerizable formulation consisting of an optimized system of monomer, surfactant, and photoinitiator, which could be used in combination with lithography-based AMT. As photopolymerization of HIPEs has been only sparingly described, thermally induced processes should be employed first to find a suitable formulation. Since acrylates are known to have significant polymerization

shrinkage and lead to rather brittle materials, thiol chain transfer agents have been added to lower the crosslink density.^[21] The resulting thiol-ene polymerization with a mixed step growth/chain growth mechanism reduces the modulus but significantly toughens the materials,^[19] thus providing a new class of resins for lithography-based AMT.

Combining the techniques of emulsion templating and AMT provides an improved, hybrid technique for the generation of four or even more levels of porosity within a polyHIPE material. Hierarchical porosity of a polyHIPE material, with its primary pores (cavities) in place of the droplets of internal phase of precursor emulsion, secondary pores interconnecting primary pores and tertiary pores between the polymer chains, is thus upgraded with another level of macro porosity.

2. Results and Discussion

For testing the applicability of HIPE templating within AMT, trimethylolpropane triacrylate (TMPTA) was initially chosen as a monomer since it exhibits good response to photopolymerization^[22] and appropriate viscosity for AMT.^[23] Since thermal polymerization is more commonly used for polymerization of HIPEs, the aim of the first experiments was to optimize a thermally initiated TMPTA-based formulation and then simply change the initiator.

A water in oil (w/o) HIPE was first tested for the preparation of polyHIPEs from TMPTA. In this case, the monomer is included in the continuous phase while aqueous phase is used to template the first level of porosity. Applying the water-soluble initiator potassium peroxydisulphate (PPS) resulted in solid monoliths after polymerization; however, significant amount of globular structures in the cavities of polyHIPEs was observed (sample A1; Figure 1). The most probable reason for this was the migration of oligomers (containing ionic residues of the initiator) in the aqueous phase of the emulsion, partly induced by the initiator present in aqueous phase. Therefore, the initiator was replaced by an oil-soluble initiator, namely azoisobutyronitrile (AIBN). Previously, Gitli and Silverstein^[24] have shown that locus of polymerization initiation within a HIPE system with monomers in both phases significantly influences both molecular structure and morphology of the yielding material. Furthermore, initiator containing phase influenced the properties of stearyl acrylate and DVB-based polyHIPEs.^[25] Locus of initiation was also found to influence morphological features of styrene/DVB-based polyHIPEs,^[26] acrylic acid-based polyHIPEs,^[27] and structure of Pickering-type polyHIPE material.^[28,29] Thermally induced radical polymerization of formula-

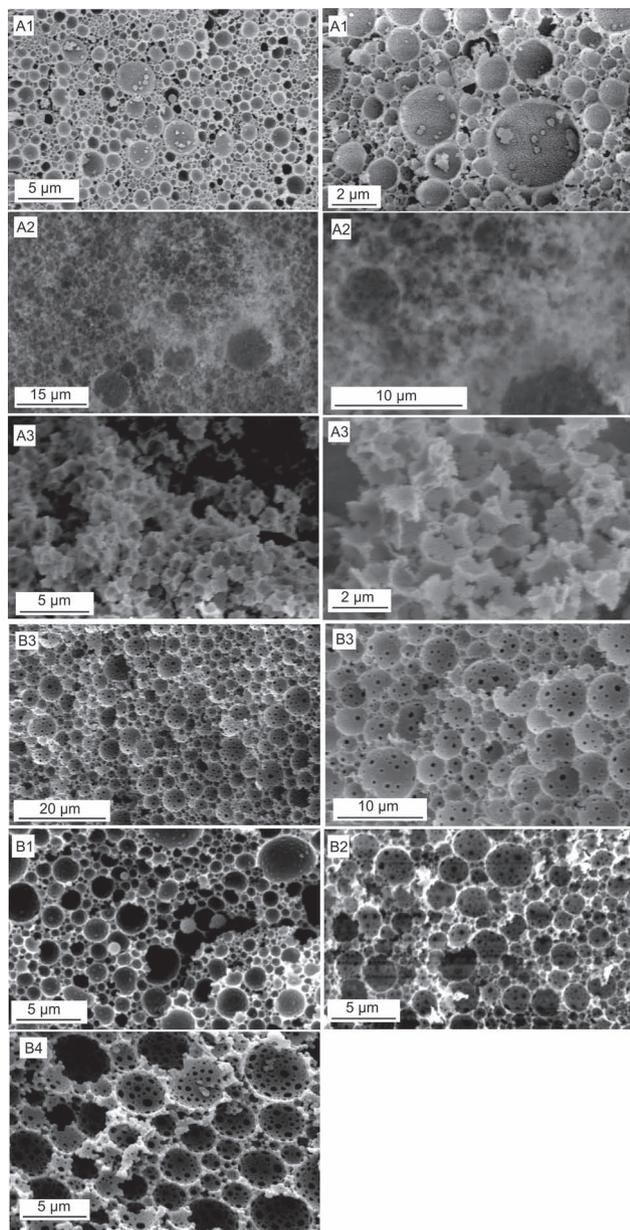


Figure 1. SEM images of polyHIPE samples.

tion A2 produced monolithic sample with typical polyHIPE morphological features (sample A2; Figure 1) with an average cavity diameter of $2.02 \mu\text{m}$ and an average interconnecting pore diameter of $0.44 \mu\text{m}$.

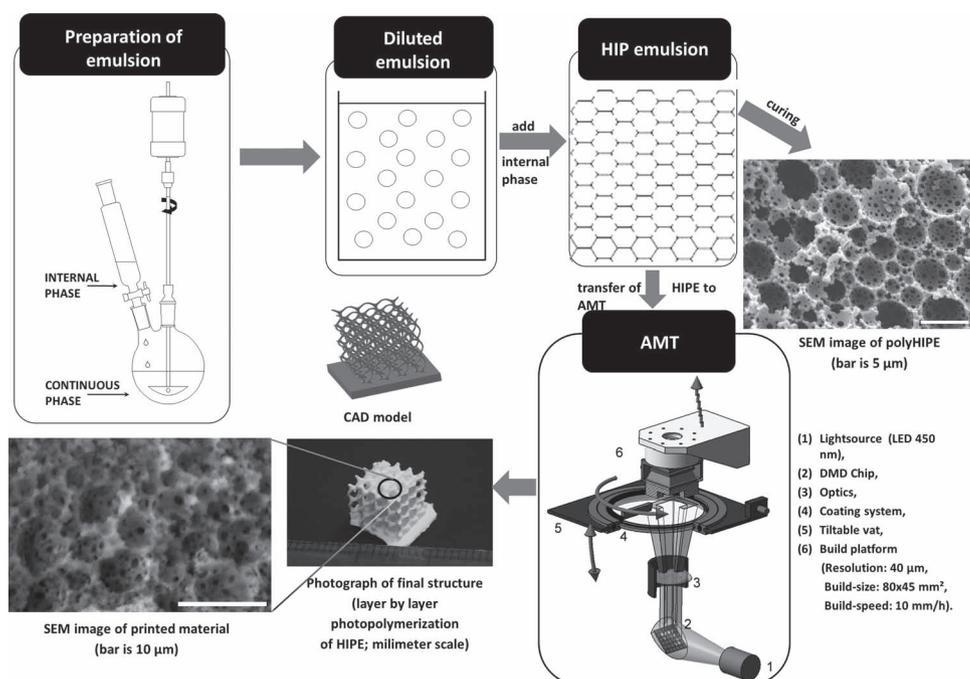
Based on prior experience with glycidyl methacrylate-based polyHIPEs,^[30] surfactants with low hydrophilic-lipophile balance (HLB) value were tested. Various combinations of surfactants PEL121 and Span65 were used and after an optimization of surfactant formulation, a mixture of 85 wt% PEL121 and 15 wt% Span 65 (with an HLB value of 1.6) provided sufficient stabilization to the HIPE during polymerization (formulation A3). Sample A3

had smaller size morphological features (cavities with $1.59 \mu\text{m}$ diameter and interconnecting pores with $0.3 \mu\text{m}$) when compared with sample A2 prepared using solely PEL121 as the surfactant.

Since the goal of this work was to polymerize HIPEs simultaneous to the printing technology (where faster polymerization is used for the polymerization of layers), we prepared the same HIPE, however replacing the thermal, oil-soluble initiator with the photoinitiator Irgacure 819. The formulation was then polymerized by exposing to UV-vis radiation ($>315 \text{ nm}$ from a metal halide bulb). Using preshaped molds (upper size of the monolith exposed to UV light), polyHIPE monoliths up to 3 mm thick were obtained. In comparison with thermally polymerized polyHIPEs, the photopolymerized HIPEs had a more homogeneous structure with almost no migration of monomers to the droplet phase (sample B1, Figure 1). Explanation could be given by the lower polymerization temperature and the faster polymerization process compared with thermal-initiated polymerization. The cavities are slightly larger (B1; $2.22 \mu\text{m}$) compared with thermally polymerized sample A3 ($1.59 \mu\text{m}$ for cavities, see Supporting Information for cavity size distribution; Figure S3). The optimized formulation from these sets of experiments was intended to be used for the structuring of polyHIPEs by lithography-based AMT (Scheme 1). The chosen layer by layer assembly method can be sensitive to viscosity.^[31] Since viscosity of HIPEs can be very high,^[32] 12.8 Pa s was measured for emulsion B1, toluene was introduced at different concentrations to dilute the oil phase and lower the viscosity. Addition of toluene (20 vol% with regards to monomers) to the TMPTA HIPE formulation (precursor emulsion for B2) lowered the viscosity to 11.04 Pa s . Addition of 50 vol% toluene reduced viscosity yet further (4.90 Pa s for HIPE B3). While there was initial concern in using such high concentrations of toluene, no detrimental effect on the polyHIPE structure was observed. On the contrary, emulsions containing toluene provided monoliths with higher pore size uniformity (sample with 20 vol% toluene) and similar or higher BET specific surface area ($53.7 \text{ m}^2 \text{ g}^{-1}$ for the sample (B3) with 50% toluene and $26.7 \text{ m}^2 \text{ g}^{-1}$ for the sample with 20% toluene (B2) versus $26.9 \text{ m}^2 \text{ g}^{-1}$ for the sample without toluene (B1).

Despite high porosity, (80% nominal) polymers were mechanically stable, exhibiting Young's moduli (60 MPa at $20 \text{ }^\circ\text{C}$ for sample B2) higher than styrene-based polyHIPE material of similar porosity.^[33]

The optimized formulation (precursor emulsion for B3) was then used for AMT (Scheme 1) with only minor modification; initiator was replaced by Irgacure 784 or the new cleavable germanium-based Type I photoinitiator Ivocerin,^[34] which better absorb the 460 nm high-power light-emitting diode (LED) light source. First attempts of



■ Scheme 1. Procedure for preparation of printed polyHIPE material.

printing the formulation, however, revealed problems with the speed of polymerization (fast polymerization hindered the formation of monolith with AMT procedure as it started to form prior to the printing process) and the amount of initiator was subsequently reduced from 0.5 to 0.1 wt%. Furthermore, a UV light absorber, Tinuvin Carbo-protect (0.1 wt%), was used to limit the penetration depth of the light and therefore improve the final resolution. The use of formulation with TMPTA, Ivocerin, Tinuvin Carboprotect, toluene (precursor emulsion for B3) resulted in successful printing of stable 3D structures. Next, an STL file containing a rectangular block of 17.25 mm x 17.25 mm x 13.88 mm with cubic close-packed overlapping spherical voids (2.30 mm) was used to steer the stereolithographic-based printer. Following solvent removal and washing, the hierarchically porous polyHIPE free standing object/Scheme 1) was ready for further testing. Scanning electron microscopy (SEM) was used to investigate the internal morphology of the printed structure. Printing did not significantly affect the polyHIPE morphology (see Scheme for SEM image). Despite very high porosity (approximately 95%), printed structures were surprisingly mechanically stable and manageable for normal handling.

In addition to the aforementioned acrylate-based HIPE, a thiol-ene-based composition was developed to demonstrate flexibility of the HIPE templating/CAD-CAM printing hybrid approach and provide materials of high toughness.^[35] The thiol-ene reaction has been used for the

preparation of polymers since the early 1940s^[35]; however, the reaction is less known for the preparation of polymers in porous systems such as HIPE. Recently, Lovelady et al.^[20] and Sergent et al.^[36] reported on the preparation of thiol-ene-based polyHIPE material. With the introduction of multifunctional thiols to the acrylate formulation, a mixed chain growth/step growth polymerization proceeds and by changing the structure of the multifunctional thiol the polymer architecture can be altered. By using a multifunctional thiol, the toughness could be improved while keeping the reactivity at high level.^[37] For our purpose, pentaerythritol tetrakis-3-mercaptopropionate was added to the previously optimized formulation of TMPTA HIPE. 20 mol% of thiol groups in relation to vinyl groups was used resulting in no apparent change in emulsion stability. Solvent and surfactant concentration were modified in a similar manner as the thiol-free emulsion (sample B4, Table 1). A comparison of morphological features shows a smaller average cavity size (3.59 μm in the case of B4 and 4.10 μm in the case of B3) and a more open structure (Table 1, Figure 1). Dynamic mechanical analysis (DMA) reveals a lower Young's modulus compared with TMPTA alone (45 MPa in the case of TMPTA/TT and 60 MPa in the case of TMPTA). Similar to the TMPTA formulation, the TMPTA/TT formulation was also compatible with stereolithographic printing. In comparison with the stable but fairly brittle material based on TMPTA, the TMPTA/TT hierarchically porous structure appeared more flexible.

Table 1. Morphological data and composition of polyHIPE samples.

Sample ID	Organic phase content	D ^{a)} [μm]	d ^{a)} [μm]
A1	PEL 121 TMPTA	1.1	/
A2	PEL 121 TMPTA AIBN	2.0	0.4
A3	PEL121 Span 65 TMPTA AIBN	1.6	0.3
B1	PEL121 Span 65 TMPTA I819	2.2	/
B2	PEL 121 Span 65 TMPTA I819 TOL	2.2	0.4
B3	PEL 121 Span 65 TMPTA I819 TOL	4.1	0.2
B4	PEL 121 Span 65 TMPTA I819 TT TOL	3.6	1.5

^{a)}D presents cavity diameter, d presents interconnecting pore diameter.

3. Experimental Section

3.1. Materials

TMPTA (Sartomer), pentaerythritoltetrakis 3-mercaptopropionate (TT, Sigma–Aldrich), toluene (TOL, Sigma–Aldrich), PPS (Fluka), azobisisobutyronitrile (AIBN, Fluka), Irgacure 819 (I819, BASF), Irgacure 784 (I784, BASF), Tinuvin Carboprotect (BASF), Ivocerin (Ivoclar Vivadent), calcium chloride (CaCl₂, Sigma–Aldrich), poly(ethylene glycol)-block-poly(propylene glycol)-block-poly(ethylene glycol) (PEG-PPG-PEG, Pluronic L121, HLB = 1.5, Sigma Aldrich), sorbitan tristearate (Span65, HLB = 2.1, Merck), and ethanol (Merck) were all used as received.

3.2. Preparation of Emulsions and polyHIPE Materials

Monomers (TMPTA and in some cases TT), initiator (0.1, 0.5, or 1 wt% to monomer), surfactants (20 or 30 vol% to monomer; Pluronic L-121, Span 65) and in some cases toluene (0, 20, or 50 vol% to monomers) were placed in a three-necked, 250-mL round bottom flask and fitted with an overhead stirrer. The aqueous phase was prepared separately by dissolving 1 wt% of CaCl₂ in water and was added over 15 min dropwise to the stirring (250 rpm) organic phase. Stirring was continued for another 30 min after the addition of the aqueous phase. Emulsions undergoing thermal polymerization were transferred to polyethylene molds and heated in an oven at 60 °C for 24 h. Emulsions undergoing photopolymerization were transferred to silicone molds and polymerized in a UV chamber (Intelliray 600, Uvitron) at 80% intensity for 120 s. Emulsions were printed with a lithography-based AMT system^[38] using a layer thickness of 25 μm and a printing speed of 2 vertical mm h⁻¹. Polymers were purified with Soxhlet extraction in water for 24 h and in ethanol for 24 h. Emulsion compositions are reported in Table S1 in Supporting Information.

3.3. Printing Procedure

The utilized lithography-based AMT system is based on a digital mirror device (see Scheme 1), which is illuminated by a high-power LED. The photosensitive-build material is first added to a vat attached to a tiltable base. To process highly viscous materials, the system is equipped with an active recoating system. After one layer is exposed, the build platform is lifted and the vat rotated in order to move fresh resin into the exposed area. The build platform is then lowered until a gap between the bottom of the vat and the previously built part is left. The thickness of the gap corresponds to the layer thickness. For the presented work, a layer thickness of 25 μm was used. After repositioning, a new layer can be exposed, which sticks to the previous layer as well as to the vat. The vat is covered with a thin layer of Teflon and a silicone film, allowing the freshly polymerized material to adhere more strongly to the previously built part and not to the vat.

3.4. Measuring the Viscosity of Emulsions

Viscosity was measured with Anton Paar Physica MCR 300 rheometer. Cone-plate CP 25-1 probe was used. The numbers refer to diameter (25 mm) and angle (1°). Sheer sweep experiments were performed at 20 °C from 0.01 to 250 Hz. Temperature sweep experiments were performed from 20 to 60 °C and back to 20 °C at 10 °C min⁻¹ rate and constant sheer of 5 Hz.

3.5. Structural Characterization of the Monoliths

The samples for SEM were prepared by fracturing in liquid nitrogen, covered with Au and characterized using low-vacuum SEM on a Quanta 200 3D (FEI Company) from 10 to 15 kV. Nitrogen adsorption/desorption experiments were carried out on a TriStar II 3020 porosimeter (Micromeritics). The average cavity sizes of prepared samples were determined from SEM images by measuring at least 50 cavities or interconnecting pores per image, using a correction factor $2/\sqrt{3}$ to compensate for the statistical error.^[14] The same procedure was used for measuring interconnecting pore sizes.

4. Conclusion

It is demonstrated that a HIPE templating approach can be used in combination with a computer-controlled layer by layer photopolymerization process. The hybrid technique is applicable to multifunctional acrylate and thiols to provide polyHIPE material with a predetermined monolithic structure. Photo-based AMT adds another level of porosity on a millimeter scale while maintaining the typical polyHIPE morphological features. This combined technique presents new options in the field of hierarchically porous polymer preparation.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements: The financial support of the Ministry of Science, Higher Education and Technology of the Republic of Slovenia (Centre of Excellence PoliMaT) through the contract No. 3211-10-000057 is gratefully acknowledged. Slovene Human Resources Development and Scholarship Fund is acknowledged for scholarship to M.S. Thanks also to Klaus Cicha and Tonica Bončina for SEM measurements and Ruth Felzmann and Simon Gruber for help with the AMT system. Ivoclar Vivadent is acknowledged for a sample of Ivocerin.

Received: January 9, 2013; Revised: March 12, 2013; Published online: April 19, 2013; DOI: 10.1002/marc.201300016

Keywords: additive manufacturing technologies; polyHIPE; porous polymers; photopolymerization; thiol-ene chemistry

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