J. Coat. Technol. Res., **4** (4) 505–510, 2007
DOI 10.1007/s11998-007-9059-3

BRIEF COMMUNICATION

Photopolymers for rapid prototyping

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Abstract Rapid prototyping by means of stereolithography using different types of photopolymers has gained increasing interest because cellular structures can be built at a high resolution with sub-μm feature sizes. Structures made with digital light processing and microstereolithography and rapid prototyping based on two-photon absorption photopolymerization techniques are presented. Soluble photopolymers were developed to substitute crosslinked photopolymers as mold materials and to extend the variety of materials which can be cast. With these molds, the processing of 'bio-inspired' ceramic composites with a controlled architecture from a macroscopic scale down to the nanometer range is possible. Another example is the development of biophotopolymers that are based on commercially available reactive diluents and modified gelatin for the fabrication of cellular bone replacement materials. Biocompatibility was investigated by seeding with osteoblast-like cells.

Keywords Photopolymers, Rapid prototyping, Biophotopolymers, Digital light processing, Microstereolithography, Two-photon polymerization

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Introduction

Rapid prototyping (RP) is a suitable manufacturing method for structures with a high geometric complexity and heavily undercut features, which cannot be fabricated easily with traditional manufacturing methods. RP techniques, such as fused deposition modeling (FDM),[1,2] selective laser sintering (SLS),[3] three-dimensional printing (3DP),[4,5] and stereolithography (SLA), have already been used in a number of applications for the fabrication of polymeric and ceramic cellular solids. Besides the classic laser-based SLA technique, alternative processes[6,7] using digital mask generators (e.g. liquid crystal displays or digital mirror devices (DMD)) have been used successfully to build structures out of polymers and ceramics.[8,9] The main advantage of using lithographic processes is the high-feature resolution which can be achieved, unlike with other RP processes. In particular, by using two-photon absorption (TPA) photopolymerization, parts with a resolution significantly lower than 1 mm can be built. The results obtained with conventional SLA, microSLA, and TPA, using novel resin formulations with specifically tailored properties, will be presented.

In a current project, the authors aim at the development of new acrylate-based biocompatible and biodegradable formulations for cellular implants. Figure 1 describes the planned overall pathway toward cellular biocompatible bone replacement materials using rapid prototyping.

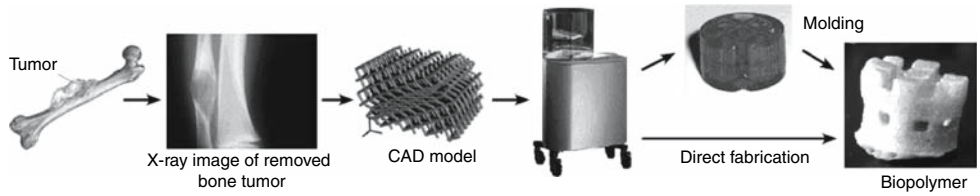

Fig. 1: Pathway toward cellular biophotopolymers

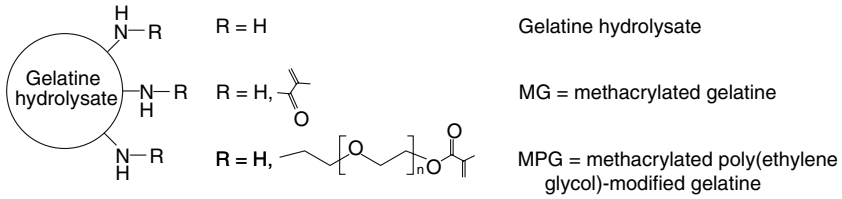

Fig. 2: Modified gelatine

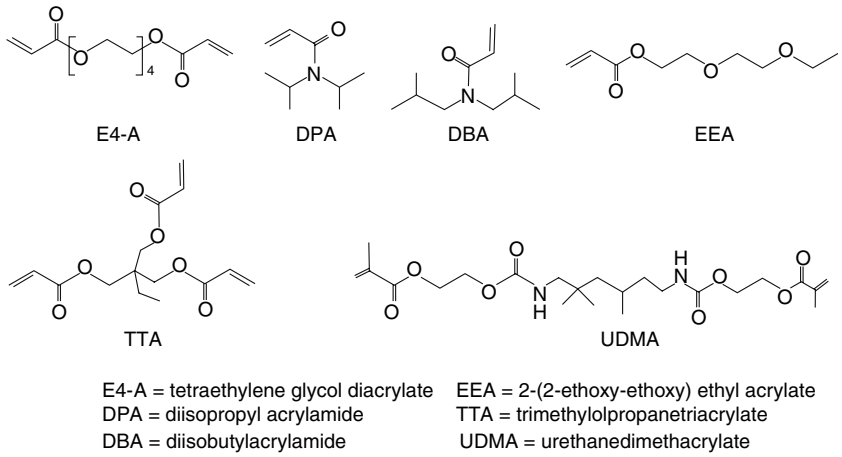

Fig. 3: Biocompatible monomers

Development of biophotopolymers

Biologically degradable polymers that are already in clinical use are usually based on polyesters such as poly(ε-caprolactone) or poly(α-hydroxy acids), e.g., copolymers of lactic and glycollic acid. These polyesters cannot be used in cases of larger defects—for example, after the removal of a bone tumor, because of their hydrolytic degradation, which causes quite a fast loss in mechanical strength. Moreover, the locally high concentration of free acids can result in tissue necrosis.

To overcome the problem of uncontrolled hydrolytic cleavage of ester-containing monomers, biodegradability is introduced here by acrylamide-based crosslinkers that can be cleaved enzymatically in vivo. In contrast to the polyesters, which can only be processed by solvent or melt techniques, only acrylate or acrylamide-based formulations are suitable for fast and UV-controlled curing using rapid prototyping.

To tune the material properties regarding processability, biocompatibility, as well as mechanical and degradation properties, several components such as a basic crosslinker, reactive diluents, fillers, and initiators have been considered.

A methacrylamide-modified gelatine hydrolysate with additional moieties for improved organo-solubility (see Fig. 2) can be used as the *base crosslinker*, which should also support the attachment and proliferation of bone-building cells.

The processing properties of the formulation and the network density of the polymer can be tuned by *reactive diluents*. A variety of commercially available photocurable monomers (see Fig. 3) were tested concerning reactivity (photodifferential scanning calorimetry—see Fig. 4), biocompatibility (cell seeding experiments with MG63 osteoblast-like cells—see Fig. 5), and mechanical properties (dynamical mechanical analysis and bending strength test—see Figs. 6 and

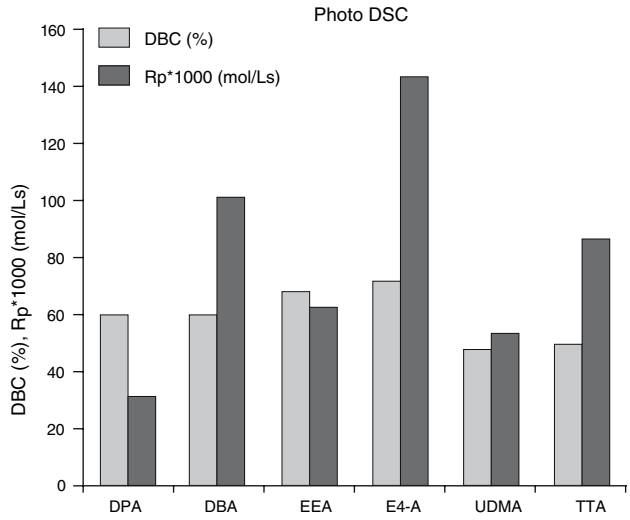

Fig. 4: Photoreactivity

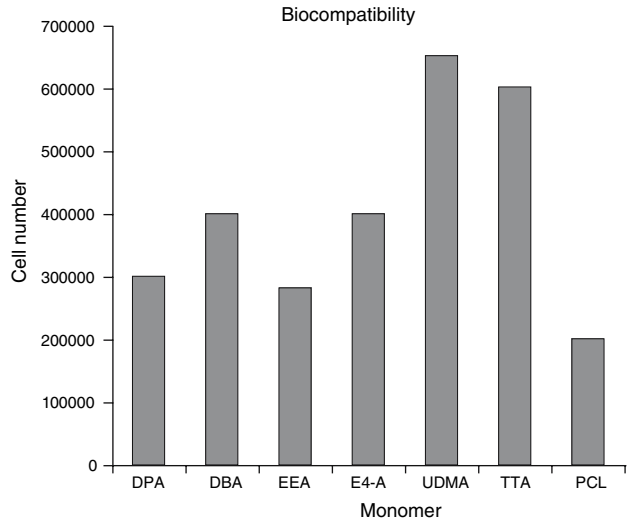

Fig. 5: Biocompatibility

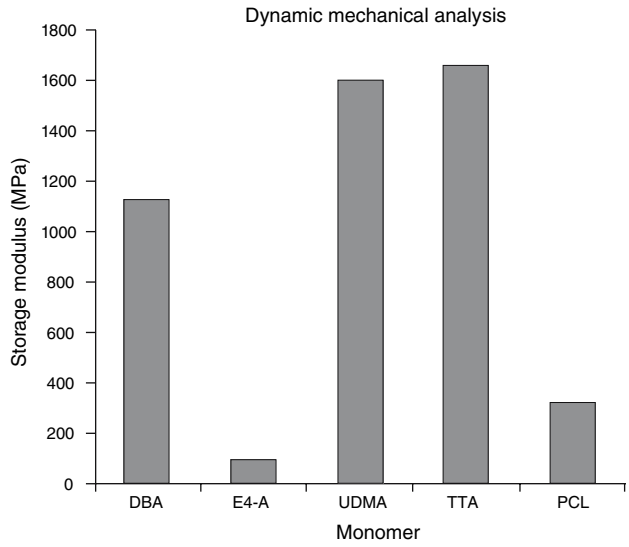

Fig. 6: Storage modulus

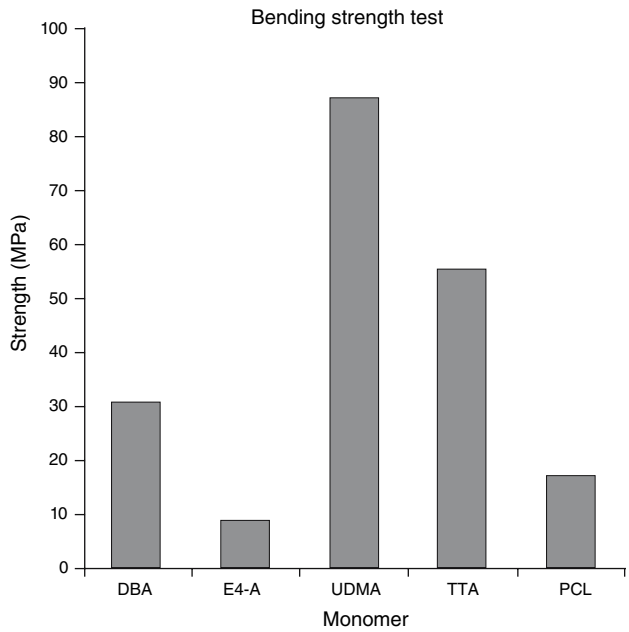

Fig. 7: Stiffness

7). Diisobutylacrylamide (DBA), trimethylolpropanetriacrylate (TTA), and urethanedimethacrylate (UDMA) appeared to be quite promising candidates because of their good results in all criteria compared with the performance of the usually applied thermoplast poly(ε-caprolactone) (PCL).

The *photoinitiating system* (see Fig. 8) consisting of camphorquinone (CQ) and *N,N*-dimethylaminobenzoic acid ethyl ester (DMAB) was selected for the preparation of test specimens of the monomers because of its known biocompatibility.[10] To tune the absorption characteristics, bisacylphosphine oxides (Irgacure 819) and hydroxyalkylphenones (Irgacure 2959), as well as the new 1,5-diphenyl-1,4-diyn-3-one (Diinone),[11] were also found to be suitable in photoreactivity and biocompatibility.

Soluble filler materials such as poly(vinyl alcohol) or cellulose acetate butyrate showed appropriate biocompatibility and can be applied to tune the viscosity for an optimum resolution of the stereolithographic shaping process. *Inorganic fillers* such as hydroxyapatite and β-tricalciumphosphate have already been described to be osteoconductive[12] and can be used to improve the mechanical properties of the polymer.

Soluble photopolymers

Commercial light-sensitive resins for the rapid prototyping of cellular materials are often unsuitable for different molding techniques because the removal of

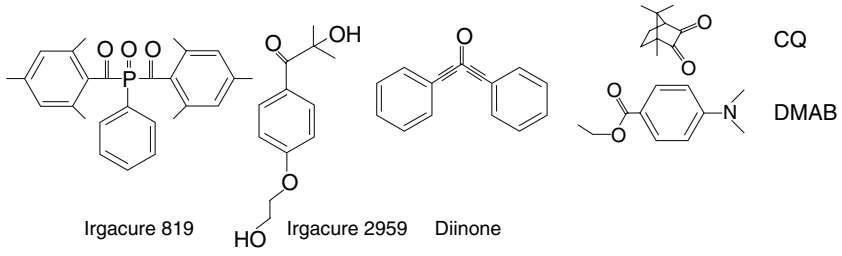

Fig. 8: Biocompatible photoinitiators

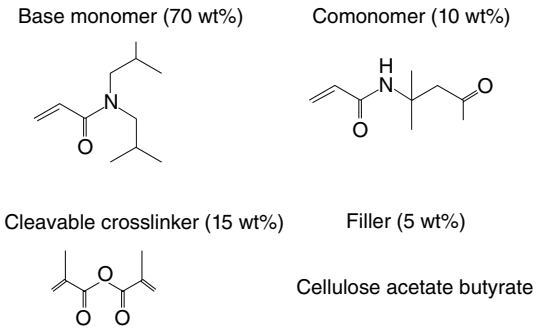

Fig. 9: Formulation for organo-soluble photopolymers

the mold uses thermal decomposition at temperatures of up to 600°C. For molding thermo-sensitive sol–gel materials or biopolymers, photocurable resins were developed, which result in organo-soluble polymers that are stable in an aqueous environment.[13]

From a wide variety of suitable monofunctional monomers, diisobutylacrylamide (DBA) was chosen as a suitable base monomer because of the high reactivity and good mechanical properties and solubility of the formed polymer (see Fig. 9). To tune the formulation with respect to the resolution, mechanical properties, solubility, and shrinkage, a series of experiments with different comonomers were carried out. Diacetone acrylamide (DAA) was found to be highly reactive and very soluble as a comonomer. A cleavable crosslinker based on methacrylic anhydride was also found to be necessary for improved mechanical properties and significantly reduced the swelling of the polymer in the monomer formulation. The use of 1 wt% Irgacure 819 turned out to be sufficient for high reactivity (t_{max}) and double-bond formation conversion (DBC).

Digital light processing (DLP)

In Fig. 10, the principle of digital light processing (DLP) is shown. For the fabrication of 3D parts, the CAD model was sliced and every slice was projected onto the bottom layer of the resin tank by a micro-mirror array. Here, the first layer of the light-sensitive resin cured in a few seconds. The polymer adhered to the *z*-stage, which was then moved upwards by 30 μm.

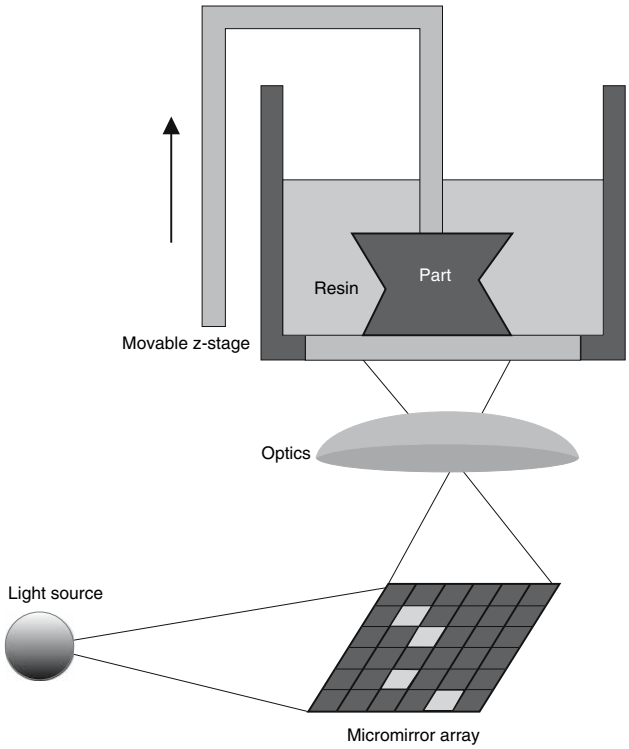

Fig. 10: Working principle of DLP

Then the next layer was cured. The feature resolution was 50 μm in the *xy*-plane and 30 μm in *z*-direction. With this technique, three-dimensional cellular organo-soluble parts were built (see Fig. 11).

Such organo-soluble molds proved to be suitable for the shaping of materials derived from water-based sol–gel processing. In this way, hierarchically structured organic–inorganic hybrid materials were shaped.[14] Figure 12 shows the wet nanostructured silica gel after the mold was removed. Figure 13 shows a molded part made from a biocompatible polymer formulation based on UDMA (see Fig. 3).

Microstereolithography

With UV-laser microstereolithography, higher resolutions can be achieved compared with DLP. The process

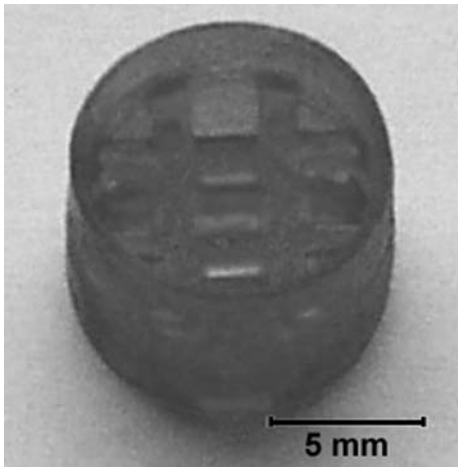

Fig. 11: Organo-soluble mold

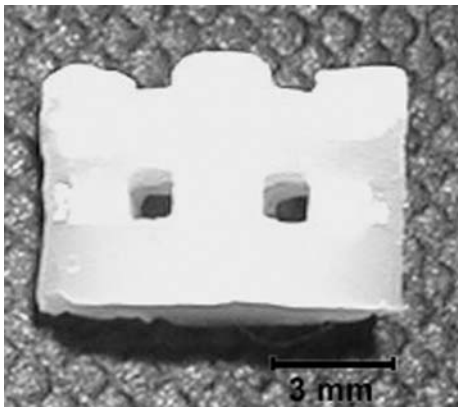

Fig. 12: Molded nano-structured wet silica gel

involves the photocuring of polymer parts in layers by moving a laser beam on the surface of a liquid monomer formulation.

Figure 14 shows a cellular 3D structure that was built by UV-laser microstereolithography. Once a layer was completely traced, the z-stage with the substrate was moved downwards by 10 μm, covered with the new resin and the next layer was cured. The resolution of this device was approximately 5 μm in the xy-plane and 10 μm in the z-direction.

Two-photon polymerization (2PP)

The two-photon polymerization (2PP) process employs femtosecond laser pulses of 800 nm which are focused onto the volume of a photopolymer, being transparent at the laser wavelength. Solidification is performed in a highly localized volume because of the quadratic dependence of the two-photon absorption probability on the laser intensity. When two photons of 800 nm are absorbed simultaneously by a suitable photoinitiator,

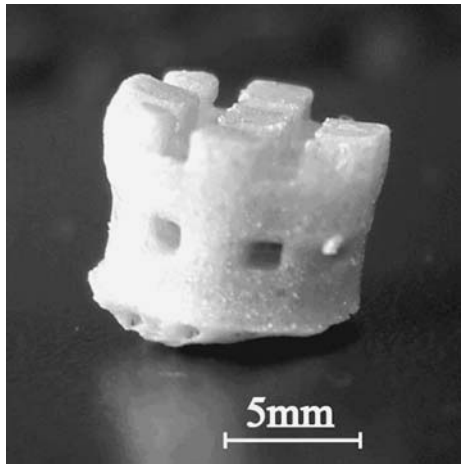

Fig. 13: Molded cellular biopolymer

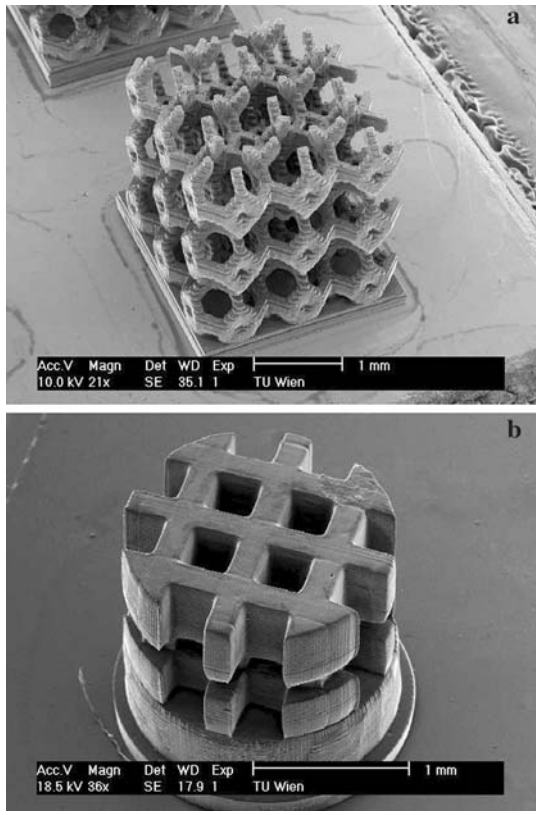

Fig. 14: Parts built by microstereolithography

they act as one 400 nm photon to start polymerization (see Fig. 15). With the 2PP feature, resolutions below the diffraction limit of the used light are possible (Fig. 16).

Recently, the authors have found a new cross-conjugated photoinitiator for 2PP which makes it possible to build parts out of a biocompatible monomer formulation based on TTA (see Fig. 3) at a photoinitiator concentration below 0.005 wt% (see Fig. 17).

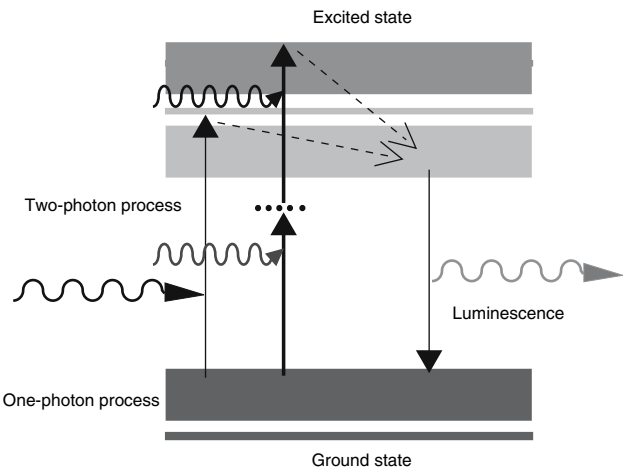

Fig. 15: Two-photon absorption (TPA)

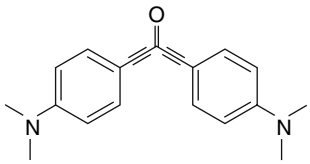

Fig. 16: Diinone-based TPA initiator

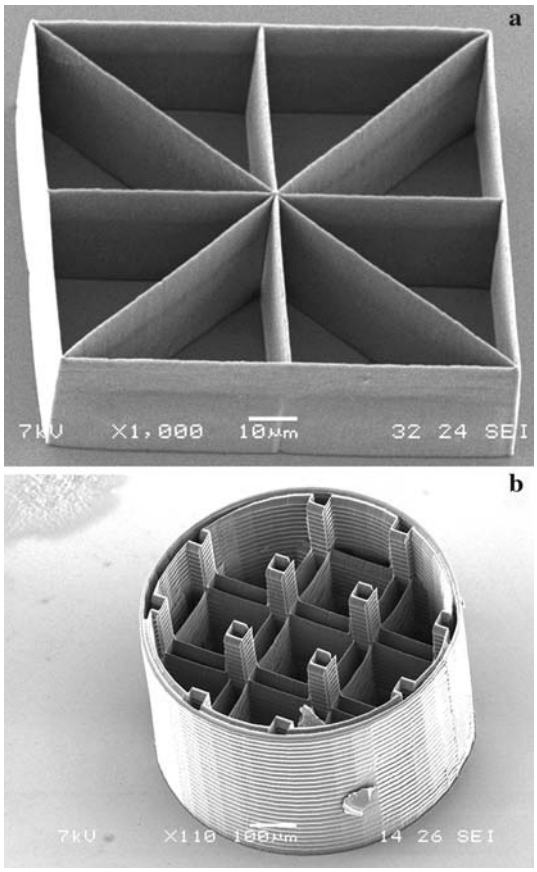

Fig. 17: Parts built by 2PP

Acknowledgments UDMA was provided by Ivoclar Vivadent AG, and photoinitiators were from Ciba Specialty Chemicals. The financial support was provided by the 'Austrian Nano Initiative' under contract No. N-703 and it and the TU innovative project '3D-Microfab' are kindly acknowledged. H. Lichtenegger thanks the Austrian Science Fund (FWF) for their financial support under contract No. T190. R. Liska thanks the FWF for financial support (P18623-N17).

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