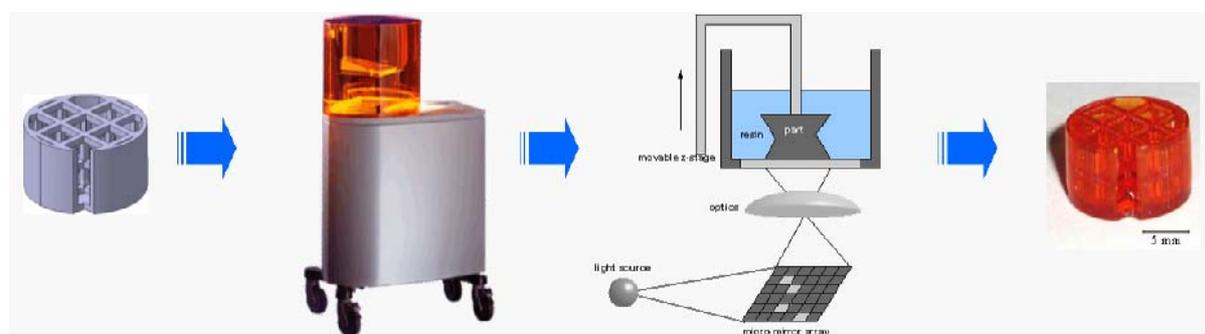


## 3D Lithography of Organo-Soluble Mold Materials for Sol-Gel Nanocomposites

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### Introduction

Rapid Prototyping (RP) is a suitable manufacturing method for fabricating structures with high geometric complexity and heavily undercut features, which cannot easily be fabricated with traditional manufacturing methods.<sup>1</sup> In Scheme 1 the direct light processing (DLP) based machine Perfactory® (Envisiontec) is shown. For fabrication of 3D parts the CAD model is sliced up and every slice is projected into the bottom layer of the resin tank by a micro-mirror array. The light sensitive resin is cured in a few seconds and peeled off afterwards. The polymer adheres on the z-stage which is moved up 30 to 50 µm in z-direction. Then the next layer is cured. By this technique 3 dimensional parts made out of polymers can be built. Commercial RP resins lead to highly cross-linked polymers. If other materials are desired the polymers have to be used as mold materials. Unfortunately they can only be removed at higher temperatures by burning, which limit the range of casting materials. Recently, water-soluble photopolymers were developed<sup>2</sup> but mold processing cannot occur in the presence of water such as for water based ceramic slurries or sol-gel materials.



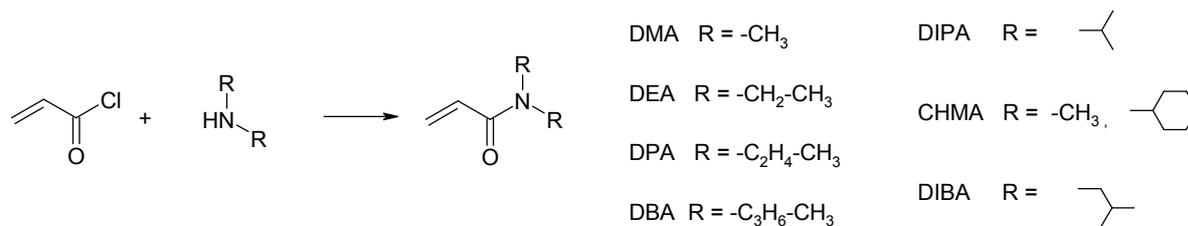
**Scheme 1:** RP-process

In the present paper the development of a photopolymerizable formulation for organo-soluble polymers is described. As suitable photoreactive base components dialkylacrylamides were selected due to their high reactivity and liquid state. In Scheme 1 an organo-soluble part built by RP is shown.

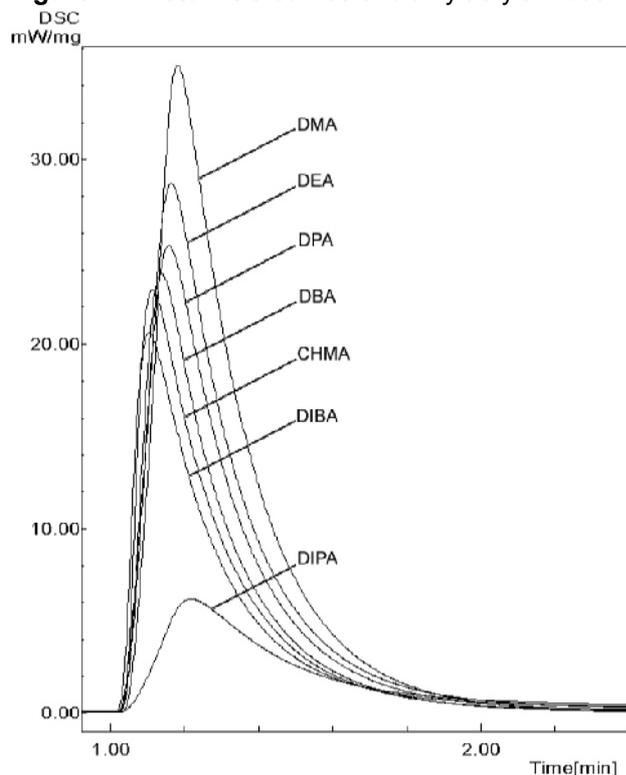
### Selection and synthesis of monomers

For the development of organo-soluble photopolymers it was necessary to find a suitable highly reactive base monomer that forms an organo-soluble hydrophobic polymer. Moreover, low shrinkage during polymerization, little swelling of polymer in monomer and good mechanical properties of the polymer were important.

As N,N-dimethylacrylamide (DMA) is a highly reactive monomer and was used in formulations that lead to water-soluble photopolymers<sup>2</sup> different dialkylacrylamides with growing side chains were considered as suitable components. With longer side chains of the monomers hydrophobicity of the formed polymer should increase (DMA < DEA < DPA < DBA; Scheme 2) while branched or cyclic side chains should improve the mechanical properties (DIPA, CHMA, DIBA). Apart DMA, which is commercially available, the investigated monomers were synthesized by reaction of 1 equivalent acrylic acid chloride with 2 equivalents of dialkylamine (Scheme 2). The products were purified by distillation in vacuo.<sup>3</sup>

**Scheme 2:** Synthesis of dialkylacrylamides**Photo-DSC**

By photo-DSC the dialkylacrylamides were investigated for their suitability as components of photocurable resins for Direct Light Projection (DLP) stereolithography. Photo-DSC was conducted with a modified Shimadzu DSC 50 equipped with a home-made aluminum cylinder.<sup>4</sup> Filtered UV-light (400-500 nm) was applied by a light guide (Efos-Novacure) attached to the top of the aluminum cylinder. The light intensity at the tip of the light guide (100 mW/cm<sup>2</sup>) was measured by an internal radiometer. The measurements were carried out in an isothermal mode at room temperature under air with 0.5 wt% of a bisacylphosphin oxide based (I819) photoinitiator (PI). The mass of the samples was 5.0 ± 0.2 mg. The time to reach the maximum polymerization heat ( $t_{max}$ ), the double bond conversion (DBC) and the rate of polymerization ( $R_p$ ) were determined.<sup>4</sup> A theoretical heat of polymerization for the calculation of the DBC and  $R_p$  was assumed for acrylamides to be  $H_0=80.5$  kJ/mol. Generally, most acrylamides showed sufficiently high reactivity, which is important for stereolithographic applications.

**Figure 1:** Photo-DSC curves of dialkylacrylamides**Table 1:** Photo-DSC data of dialkylacrylamides

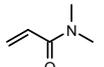
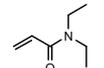
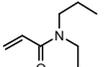
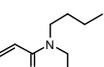
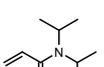
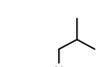
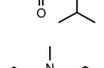
monomer	abbr.	$t_{max}$ [s]	DBC [%]	$R_p$ [mol l <sup>-1</sup> s <sup>-1</sup> ]
	DMA	10.8	78	0.46
	DEA	10.2	83	0.35
	DPA	9.6	82	0.28
	DBA	8.4	84	0.26
	DIPA	18.0	63	0.11
	DIBA	6.6	75	0.23
	CHMA	7.2	72	0.28

Table 1 shows that the acrylamides with linear side chains had similar values for DBC whereas the DBC of the branched acrylamides was lower. Except the sterical hindered DIPA (Figure 1) the branched monomers showed a higher reactivity ( $t_{max}$ ), which can be explained with a higher degree of order in the branched monomers.

## Properties of the polymers

Apart from the photopolymerization activity of the monomer, also mechanical properties and solubility of the polymer had to be considered. Test specimens (60 x 10 x 3 mm) were prepared by irradiation of the formulation in a suitable silicone mold. For this set, 0.5 wt% I819 was chosen as PI to ensure entire curing also in deeper layers. Shrinkage during polymerization should be low to obtain good feature resolution during RP process. Calculation was done by comparison of monomer and polymer densities using the measurement of the polymers buoyancy in glycerin. Swelling of polymer in monomer during RP process should be minimal to obtain hard RP parts with suitable feature resolution. Therefore the gain of weight of a polymer in its monomer, at 50°C for 24 hours, was considered. Mechanical properties were characterized by measurement of Shore hardness D. Solubility, one of the important properties, was determined by stirring a defined specimen in THF at 50°C and determination of the time for entire dissolution.

As expected, the shrinkage during polymerization decreases with increasing molecular weights of the monomer (Table 2). In the case of the polymers of DEA, DPA, DIBA, swelling decreased with increasing side chain length of the polymers. But no exact conclusion could be made because some test specimens were so highly swollen and sticky that they could not be valued. Monomers with short linear side chains formed hard polymers. Hardness significantly decreased with growing linear side chains. Highly branched and cyclic side chains of the monomers gave hard polymers.

From previous investigations it is known that methacrylic anhydride (MSA) depicts a suitable alkaline cleavable crosslinker for water dissolvable formulations.<sup>2</sup> Improved mechanical properties, feature resolution and decreased swelling of the polymer in the monomer have been obtained. Drawbacks were the increased dissolution time. Therefore MSA was also used as a cleavable crosslinker for organo-soluble formulations. In an appropriate organic solvent like THF it can easily be cleaved by n-butylamine. Table 2 shows some properties of the homopolymers in comparison with their copolymers with 10 wt% MSA.

**Table 2:** Properties of homopolymers and copolymers

Monomer	Homopolymer				Copolymer with 10 wt% MSA		
	Shrinkage [%]	Swelling in monomer [%]	Shore hardness D [-]	Solubility [min] <sup>1)</sup>	Swelling in monomer [%]	Shore hardness D [-]	Solubility [min] <sup>2)</sup>
DMA	13.5	— <sup>3)</sup>	79	55	238	80	90
DEA	11.6	599	70	swelling	166	77	swelling
DPA	9.6	377	61	80	88	70	30
DBA	8.0	— <sup>3)</sup>	26	40	69	58	60
DIPA	— <sup>4)</sup>	268	70	10	48	74	15
CHMA	7.4	59	83	85	16	85	60
DIBA	7.8	122	73	190	19	77	65

<sup>1)</sup> ...in THF

<sup>2)</sup> ...in THF / n-butylamin (v/v=4:1)

<sup>3)</sup> ...too much swollen

<sup>4)</sup> ...not measured

## Influence of MSA concentration on copolymers of CHMA and DIBA

CHMA and DIBA were of special interest because their homopolymers showed good mechanical properties and did not swell in water which is important for the use as a mold material for aqueous systems. Therefore the concentration dependency of MSA was evaluated.

As expected swelling of the polymer in the monomer decreased by application of MSA and reached a minimum at 15 to 20 wt% of the crosslinker (Figure 2). Higher amount of MSA gave no significant improvement. By adding MSA, the hardness of the copolymer of CHMA only increased a little bit due to the similar level of about 85 shore hardness of the MSA-homopolymer. By using 5 to 15 wt% MSA significant increase of hardness for the DIBA-copolymer was observed. Surprisingly, crosslinking with MSA improved dissolution behavior of the copolymers in a mixture of THF/n-butylamine (4:1). In general good solubility could be achieved with 10 to 20 wt% MSA.

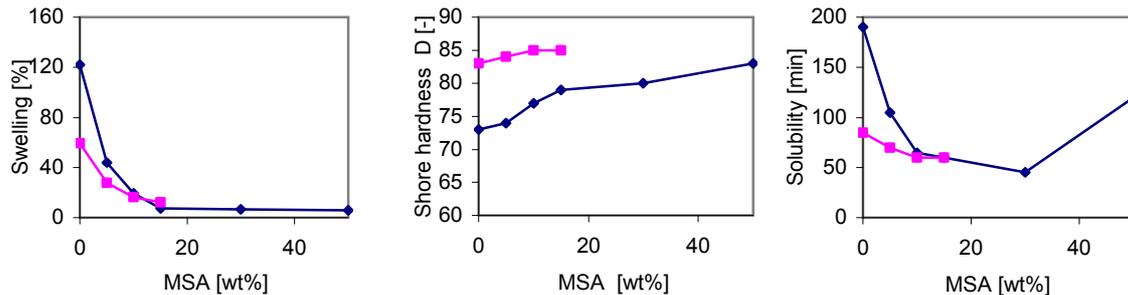


Figure 2: Properties of DIBA (—◆—) and CHMA (—■—) with different MSA concentration

## Optimization of Formulation

For further experiments DIBA was chosen as suitable base monomer because of the best overall performance. To tune the formulation with respect to the resolution, mechanical properties, solubility and shrinkage a series of experiments with different co-monomers were carried out. Diacetone acrylamide (DAA) was found to be a highly reactive and well soluble comonomer. Due to its hydrophilic properties only 10 wt% were used for formulations to build molds for aqueous mold conditions. Beside improved solubility of the mold material DAA reduced diffusion into the siliconvat. 10 to 15 wt% of crosslinker showed to be effective for improving mechanical properties and to reduce swelling of the polymer in the monomer effectively. To find the optimum PI concentration, photo-DSC experiments with 0.1 to 3.0 wt% of PI in DIBA were carried out. 1 to 3 wt% PI were sufficient for high reactivity ( $t_{max}$ ) and for almost complete double bond conversion (DBC) (Figure 3).

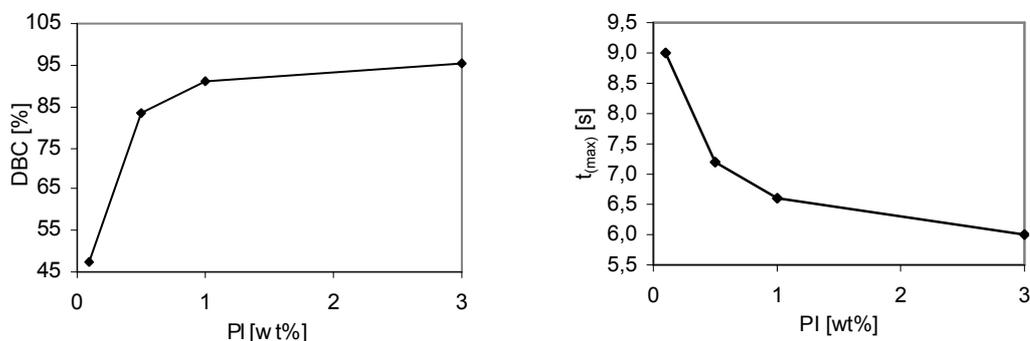


Figure 3: Photo-DSC: DBC and  $t_{max}$  of DIBA with different PI concentrations

Cellulose acetate butyrate was used to increase the viscosity of the resin, which is important for good processing properties by RP and to decrease radical diffusion. By application of a UV-VIS absorber increased feature resolution was obtained. It was found that the optimum formulation consists of 72 wt% DIBA, 11 wt% MSA, 10 wt% DAA, 4 wt% cellulose acetate butyrate, 3.0 wt% PI and 0.1 wt% UV-VIS absorber.

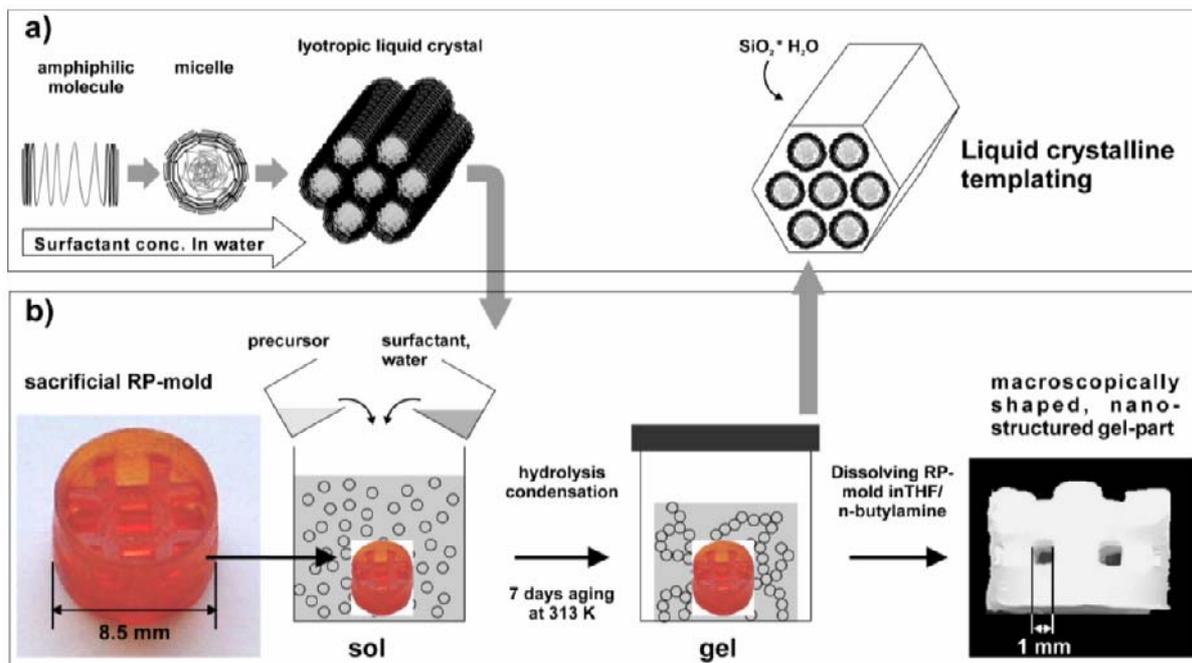
## Mold processing of sol gel materials

Natural materials such as bone, teeth or nacre are nanocomposites of proteins and minerals. This combination of soft and hard matter on the small scale results in materials with interesting mechanical properties. Generally a well defined organization of the components in the natural composite can be found. It has turned out that not only the composition but also the organization and the shape of the components in the composite play a significant role for the final mechanical properties, e.g., increased fracture toughness.<sup>5</sup>

In nature this cooperative arrangement of the components is accomplished by complex processes of self-organization. One way to mimic this is the self-assembly of amphiphilic molecules in a solvent. Self-assembled lyotropic liquid crystalline phases can be used for example as templates in the fabrication of mesostructured materials with ordered porosity (M41S materials) through sol-gel chemistry, mostly realized in films and powders.<sup>6</sup> The production of large monolithic pieces is still exception, due to inherent chemical incompatibilities in the precursor solution and shrinkage during drying. The porous M41S materials are of great interest for applications in size- and shape-selective processes (e.g., as catalysts or as host structures for nanometer-sized guest compounds) and in the meantime have also become candidates in the fabrication of nanocomposites.<sup>7</sup>

Nevertheless, the fabrication of sol-gel derived nanocomposites with a high degree of mesoscopic order in combination with complex macroscopic morphologies such as they are found in nature (e.g. bone), is rarely achieved. One reason is the difficulty encountered when making large monoliths, such as shrinkage and the general difficulty to bring mesostructured materials into complex 3-dimensional shapes. The approach used here is templating with 3-dimensional molds designed with rapid prototyping.<sup>8</sup>

The templating of organic/inorganic nanocomposites is a general challenge because of the temperature sensitivity of the organic phase that does not allow for calcination as a method for template removal. Water- and organo-soluble photo-polymerizable resins for stereo lithography RP which are dissolvable at ambient temperatures permit to macroscopically shape materials derived by soft chemistry methods (Chimie douce).<sup>9</sup> The organo-soluble resins furthermore can be applied for shaping water based systems as described in the following.



**Figure 4: a) Templating on the nano-scale:** Amphiphilic molecules are used as structure directing agents in the sol-gel fabrication of mesoporous silica leading to an ordered nanostructure.

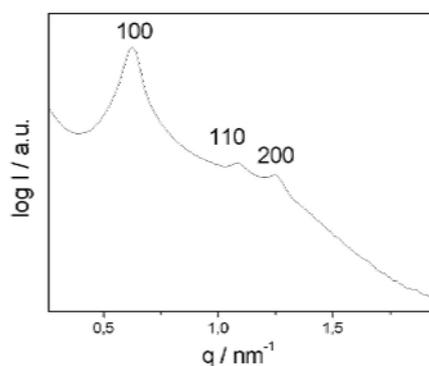
**b) Templating on the macro-scale:** Far left the sacrificial RP-mold with a simple net of struts (diameter = 1 mm). Far right the remaining macroscopically structured gel-body after gelation of the sol, aging of the gel and removal of the mold.

Monolithic, mesostructured silica with ordered porosity was derived by sol-gel-synthesis, using water-

soluble ethylene glycol modified silane (EGMS) as precursor, the non-ionic block copolymer Pluronic P123 (PEO-PPO-PEO) as structure directing agent and 1 M HCl as catalyst following the procedure described by Brandhuber et al.<sup>10</sup> leading to a hexagonal structure with a pore diameter of about 10 nm. Figure 1 b shows the procedure of gel-casting schematically.

The organo-soluble part with a diameter of 8.5 mm made by stereolithography is depicted in Figure 4b. After mixing and homogenization of the reactants the aqueous sol was immediately transferred onto the RP-mold. Self-assembly of the mesostructured silica/P123 composite took place inside the mold.

After aging of the gel for one week at 313 K in a closed vessel the mold was removed by dissolving in THF/n-buthylamine (v/v=9/1) at RT leaving the wet nanostructured gel (Figure 4b, to the right). The dissolving took 4 h, after that the gel-part was washed several times in ethanol. The obtained part shows a well resolved negative of the sacrificial polymeric structure. Figure 5 shows the nanostructure of the supercritical dried gel uncovered by small angle x-ray scattering. The peak positions can be indexed according to a hexagonal structure with  $d_{100}$ ,  $d_{110}$  and  $d_{200}$  clearly visible.



**Figure 5:** Small angle x-ray scattering pattern of the nanostructured gel (hexagonal arrangement of rod-like pores).

## Summary

In the present investigations, a formulation for organo-soluble photopolymers for RP has been developed. It has been found that branched dialkylacrylamides gave best performance towards photoreactivity, swelling in the monomer, mechanical properties and dissolution behavior. Further optimization was achieved by a cleavable crosslinker. It has been shown that the photopolymers are excellently suitable as mold materials for mesoporous sol-gel materials.

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<sup>10</sup> Brandhuber, D., et al., *Cellular mesoscopically organized silica monoliths with tailored surface chemistry by one-step drying/extraction/surface modification processes*. Journal of Materials Chemistry, 2005. **15**(Advance Article)