Poly(glycidyl methacrylate)s with controlled molecular weights as low-shrinkage resins for 3D multibeam interference lithography†

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Poly(glycidyl methacrylate) has been shown to be a useful material for fabrication of photonic crystal templates using multibeam interference lithography, since it exhibits lower shrinkage than conventional SU8.

Three-dimensional (3D) laser microfabrication techniques such as two-photon lithography[1] and multibeam interference lithography[2] offer efficient routes to fabricate many microscale structures for applications such as micro-optics, microfluidics, microelectromechanical systems, and optical data storage.[3,4] A particular class of 3D micro-optical elements of great interest are photonic crystals (PCs), which exhibit photonic bandgap (PBG) properties; that is, the propagation of photons in a range of electromagnetic frequencies is forbidden within the material. The structures are often fabricated in negative-tone photoresists, which become insoluble upon exposure to light due to crosslinking of monomers or polymer precursors initiated by photogenerated radicals or acids. Because of the relatively low dielectric contrast between typical polymers and air, the patterned polymer structures are often used as templates for backfilling with high-index materials, followed by removal of the polymer template to realize complete PBGs.[5–7] Therefore, the fidelity of the final PCs is critically dependent on that of the polymer template. Any volumetric shrinkage of the patterned polymer templates can lead to dimensional distortion, resulting in PCs with structures different from the original design and incomplete PBGs.[8] In addition, if the film is attached to the substrate, cracks may occur and propagate due to the residual strain generated from large film shrinkage, further degrading the optical quality of the PCs.

The commercially available negative-tone photoresist, SU8 (Fig. 1), has been widely used in 3D microfabrication.[9] It is a multifunctional epoxy derivative of a bisphenol-A novolac with an average of eight epoxy groups per chain[10] and has an average molecular weight of 1397 g mol^{-1}. When photoacid generators are incorporated into the SU8 resin, these materials can be polymerised and crosslinked into an infinite network through cationic ring-opening reaction upon exposure to light. However, SU8 templates often suffer from large volumetric shrinkage (as high as *ca.* 41% for a 3D diamond-like structure) after post-exposure baking (PEB) and development.[8,11] While the percentage of shrinkage can be modified by the exposure dosage, and PEB time and temperature, fundamentally the shrinkage is caused by the increase of film density during the polymerisation, in which the van der Waals separation of monomer units is replaced by covalent bonds. One approach to address this is to design highly branched multi-functional monomers such that formation of only a few bonds can lead to a dramatic switching of solubility, thus simultaneously improving viscosity and lowering film shrinkage. Dendrimeric methacrylates are examples of branched monomers;[12] however, there is generally a volume shrinkage of *ca.* 15–20% associated with the use of vinyl monomers.[13] We, therefore, sought to use an epoxy-based system with a controllable number of epoxy groups in an effort to optimize the tradeoffs between solubility of our resin for good film formation and the number of epoxy groups required to switch solubility.[14] Glycidyl methacrylate (GMA) resins have previously been shown to form films with good mechanical properties and high chemical resistance, and have been employed for coatings, printing inks, recording materials, photoresists, and printing plates.[15] Here, they were chosen as potential candidates for low-shrinkage materials and compared to that of SU8. The molecular structures of SU8 and GMA are illustrated in Fig. 1.

First, we studied the influence of the degree of polymerisation (DP) of the methacrylic backbone of the poly(glycidyl methacrylate) (PGMA) on the volumetric shrinkage of the diamond-like structure. Atom-transfer radical polymerisation (ATRP) has been used to

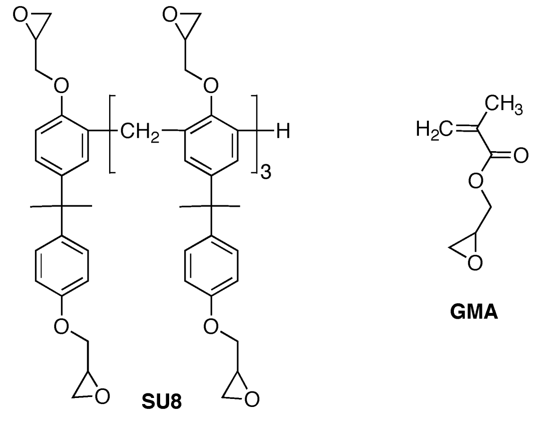

Fig. 1 Molecular structures of SU8 and of GMA.

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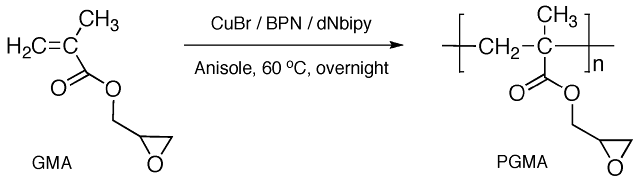

Scheme 1 Synthesis of poly(glycidyl methacrylate) *via* ATRP.

obtain glycidyl methacrylate polymers with well-controlled average molecular weights and narrow molecular weight distributions.[16,17] Accordingly, we synthesised well-defined PGMA using ATRP in anisole at 60 °C overnight, using 2-bromopropionitrile (BPN) as initiator and CuBr/dNbipy (dNbipy = 4,4′-dinonyl-2,2′-dipyridyl) as the catalytic system (Scheme 1) with a yield of *ca.* 60% (see ESI for details†). In comparison, only 50% of the monomer was polymerised after 14 h at room temperature. The conversion was determined using ^{1}H NMR spectroscopy, following the disappearance of GMA proton signals over the course of the reaction.

The polymers were precipitated from ligroin as white solids and characterized by ^{1}H NMR spectroscopy[18] and gel permeation chromatography (GPC). The molecular weight of the polymers was varied by using different concentrations of initiator (BPN) relative to monomer (GMA). Six PGMA samples were obtained with average DPs of 20, 30, 35, 45, 55 and 105. The polydispersity indices (PDI), obtained from GPC relative to linear polystyrene standards, are in the range of 1.21–1.39, which is similar to the literature value for ATRP-produced PGMA.[19]

The photoresist solution (*ca.* 27–40 wt%) was formulated in cyclohexanone (Aldrich) by mixing PGMA and 2.0 wt% Irgacure 261 ($[\mathrm{CpFe}(\eta^6\text{-}^i\mathrm{PrC_6H_5})]^+[\mathrm{PF_6}]^-$, from Ciba Specialty Chemicals) as a visible photoacid generator, and spin-coated on glass substrate at 1000–2000 rpm for 30 s.

We found that the solubility of PGMA with a relatively low DP of 35 is much higher than that of PGMA with DP of 105. At a concentration of 30 wt%, a relatively thin film (*ca.* 2–3 μm) was obtained from PGMA precursor with DP of 105, in comparison to *ca.* 5–6 μm film from DP = 35 at a concentration of 40 wt%.

To quantify the shrinkage of PGMA materials, we fabricated diamond-like structures using the same optical setup as that for SU8 by subjecting the photoresists to four umbrella-like visible laser beams split from one coherent laser source (λ = 532 nm, diode-pumped Nd:YVO$_4$ laser).[7] The films were prebaked for one minute at 65 °C, and then exposed to the superimposed interference beams (laser output of 1 W) for 3–8 s. The power of the light source for all PGMA structures was kept as 1 W, but the exposure time was optimized to give similar porosity as those for SU8 structures. IR measurements (see ESI for details†) suggest that *ca.* 7–10% of the epoxy groups of the PGMAs are cross-linked under these conditions. After a post-exposure bake at 65 °C for 2–4 min and 95 °C for 1–2 min, respectively, the films were developed in propylene glycol monomethyl acetate for *ca.* 30–40 min to remove unexposed or weakly exposed films, followed by soaking in isopropanol for 5–10 min to obtain the 3D microporous structures. To prevent collapse of the patterned 3D film due to capillary forces upon air-drying, the films were dried using a supercritical CO$_2$ dryer (SAMDRI®-PVT-3D, tousimis) after the development. High-resolution SEM images were taken on a FEI Strata DB235 Focused Ion Beam system at 5 kV (see Fig. 2). The pitch in the (111) plane of the 3D diamond-like structure was measured from SEM images. Each sample was measured twice in three different directions and positions. The pitch in the (111) plane of the 3D structure was measured as the average center-to-center distance of the holes in three different directions. The distance between the adjacent lattice planes in the [111] direction was measured from the ion-milled cross-section.

The film shrinkage was estimated by comparing the measured lattice constants of the fabricated 3D structures from SEM with the theoretically calculated values, The detailed calculation and reconstruction of the theoretical 3D structures were reported earlier.[8]

As seen from Table 1, the 3D structure fabricated from PGMA (DP = 35) shows much lower shrinkage (18%) in the [111] direction in comparison to that from SU8, 41% (ESI† Fig. S3 and S4). In the (111) plane, while the SU8 structure was essentially unchanged, we observed 7.1% expansion for PGMA (DP = 35). Overall, the volume shrinkage of the 3D structure is 5.9% for PGMA films, much lower than that from SU8, 42%. For both PGMA and SU8 templates, the difference in shrinkage in different directions can be attributed to the substrate confinement effect, where the porous structure can shrink freely in the vertical direction but is restricted in the horizontal plane.

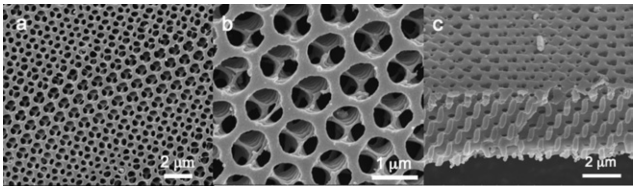

Fig. 2 SEM images for the diamond-like structure from PGMA (DP = 35). a) Large field of view. b) Top-view. c) Cross-sectional view, tilted at 45°.

Table 1 Comparison between volumetric shrinkage of PGMA (DP = 35) and SU8 under the same fabrication conditions

	PGMA (n = 1.52, DP = 35)		SU8 (n = 1.60)	
Materials	Pitch in the (111) plane	Distance between the adjacent lattice planes in the [111] direction	Pitch in the (111) plane	Distance between the adjacent lattice planes in the [111] direction
Experimental/μm	1.05	1.07	0.97	0.81
Calculated[a]/μm	0.98	1.30	0.98	1.38
Shrinkage (%)	−7.1	18	1.0	41
Volume shrinkage (%)	5.9		42	

[a] Obtained from level surface by considering the influence of refraction at the photoresist film/air interface.

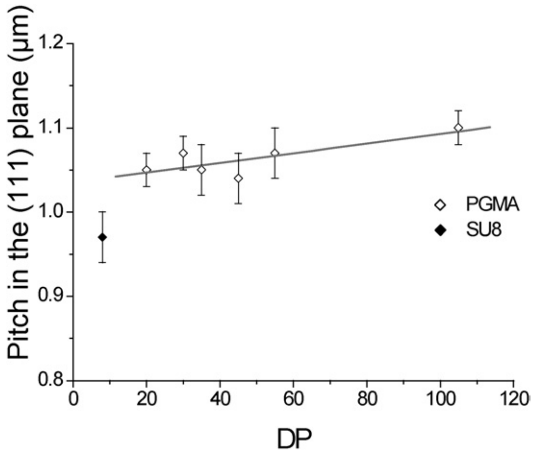

Fig. 3 The pitch in the (111) plane for 3D SU8 and crosslinked PGMA strucures *versus* the degree of polymerisation of the oligo(epoxide)s used.

In the case of SU8 material, there are an average of eight epoxy groups per monomer. However, the number of epoxy groups in the PGMA precursor can be controlled by the degree of the polymerization owing to the use of ATRP. As shown in Fig. 3, the pitch in the (111) plane increases with the DP of PGMA. Therefore, the shrinkage and periodicity of the 3D PCs can be varied to some extent by varying the molecular weight of the PGMA precursor. Compared with SU8, the PGMA materials always show a higher pitch in the (111) plane, suggesting that PGMA exhibits lower shrinkage than SU8 regardless of molecular weight; one of the possible factors responsible for this may be the higher flexibility of the PGMA polymer backbone. The lower shrinkage from PGMA precursors leads to larger lattice constant in the fabricated diamond-like structures, therefore smaller lattice distortion in comparison to that of SU8.[8] Our preliminary photonic bandgap calculations, which will be reported in detail elsewhere, suggest that the PGMA 3D structures offer better photonic bandgap quality than SU8 3D structures.

In conclusion, poly(glycidyl methacrylate)s with different molecular weights have been synthesised in a well-controlled fashion using ATRP. 3D diamond-like cross-linked structures were successfully fabricated by using PGMA precursors as photoresist through the multibeam interference lithography method. The comparison of our experimental results with the calculated values showed that the 3D PGMA structures have a lower volumetric shrinkage, 5.9%, than structures fabricated from the SU8 materials under the same conditions (42%), which may offer better control of the photonic bandgap properties of PCs templated by this material.

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