Photoprocessable Polymer Opals

Birger Lange,[†] Rudolf Zentel,*[,†] Christopher Ober,[‡] and Seth Marder[§]

Institute of Organic Chemistry, Department of Chemistry and Pharmacy, University of Mainz, Duesbergweg 10-14, 55128 Mainz, Germany, Department of Materials Science & Engineering, Cornell University, Ithaca, New York 14853, and School of Chemistry and Biochemistry and Center for Organic Photonics and Electronics, Georgia Institute of Technology, Atlanta, Georgia 30332-0400

Received July 18, 2004. Revised Manuscript Received September 28, 2004

Monodisperse colloids have been synthesized from the acid labile polymer poly *tert*-butylmethacrylate. They can be loaded with photoacid generator and crystallized into polymer opal photonic crystals. Irradiation with UV-light followed by baking and development with aqueous base allows subsequent patterning of the opaline films. This chemical approach makes it possible to use the self-assembly of this colloids (opal formation) to form a large-scale periodic structure and to introduce optical defects with UV-lithography.

Introduction

Progress in electronics and photonics can be seen in the development of new materials, which broadens our ability to manipulate electron and photon transport, respectively. Photonic crystals (PhCs) are a new class of materials first discussed in 1987. Eli Yablonovitch[1] and Sajeev John[2] introduced the idea of controlling light and its emission with photonic crystalline materials. Promising methods for the fabrication of three-dimensional (3D) PhCs[3] include self-assembly of nanospheres into opals,[4] the use of holography,[5] and two-photon lithography.[6,7] An important property of PhCs is that they have a spatially periodic varying refractive index. This leads to the formation of a photonic band structure, which can possess a complete photonic band gap for certain frequency ranges. The motivation for research in this field is to build a generation of optic devices of reduced size, combining high integration and high-speed processing.[8]

The self-assembly of monodisperse spheres into ordered 3D opal structures has recently attracted great attention, because it is possible to control the film thickness[9] and fabricate large area photonic films.[10] They can be made in their bare[11] or in an inverted form following a template approach,[12] at low cost and large scale required by mass production. The choice of material composition (SiO_2 or polymer), lattice periodicity, and symmetry as well as the possibility to create heterostructures with different lattice parameters gives control over the properties of this novel class of materials.[13−15] Progress in photonics is closely linked to the development of optical materials with tailor-made properties.

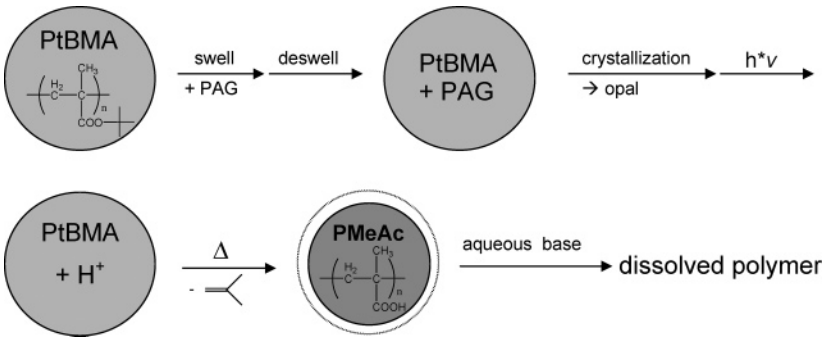
Advanced photonic circuits will need complex architectures and a sufficient number of spheres to ensure a photonic band gap effect in all directions. There are different ways to fabricate PhCs by colloidal assembly, including controlling the stages of sedimentation, using patterned substrates[12] (also grooves[16,17] and pyramid shaped pits[18,19]), or using electrically driven deposition.[20] These steps direct the crystallization to a special place, but the incorporation of defined defects (planes, lines, points) inside the opal is still hardly possible. Only the fabrication of defect-planes is already realized.[15,21] For polymer opals from methacrylates, there is in addition

* Corresponding author. Phone: +49-6131-39-20361. Fax: +49-6131-39-24778. E-mail: zentel@uni-mainz.de.
[†] University of Mainz.
[‡] Cornell University.
[§] Georgia Institute of Technology.

(1) Yablonovitch, E. *Phys. Rev. Lett.* **1987**, *58*, 2059.
(2) John, S. *Phys. Rev. Lett.* **1987**, *58*, 2486.
(3) Busch, K.; Lölkes, S.; Wehrspohn, R. B.; Föll, H. *Photonic Crystals*; Wiley−VCH: New York, 2004.
(4) Park, S.-H.; Gates, B.; Xia, Y. N. *Adv. Mater.* **1999**, *11*, 462.
(5) Campbell, M.; Sharp, D. N.; Harrison, M. T.; Denning, R. G.; Turberfield, A. J. *Nature* **2000**, *404*, 53.
(6) Cumpston, B. H.; Ananthavel, S. P.; Barlow, S.; Dyer, D. L.; Ehrlich, J. E.; Erskine, L. L.; Heikal, A. A.; Kuebler, S. M.; Lee, I.-Y. S.; McCord-Maughon, D.; Qin, J.; Röckel, H.; Rumi, M.; Wu, X.-L.; Marder, S. R.; Perry, J. W. *Nature* **1999**, *398*, 51.
(7) Sun, H.-B.; Matsuo, S.; Misawa, H. *Appl. Phys. Lett.* **1999**, *74*, 786.
(8) Joannopoulos, J. D.; Villeneuve, P. R.; Fan, S. *Nature* **1997**, *386*, 143.
(9) Gu, Z.; Fujishima, A.; Sato, O. *Chem. Mater.* **2002**, *14*, 760.
(10) Griesebock, B.; Egen, M.; Zentel, R. *Chem. Mater.* **2002**, *14*, 4023.
(11) Astratov, V. N.; Bogomolov, V. M.; Kaplyanskii, A. A.; Prokofiev, A. V.; Samoilovich, L. A.; Samoilovich, S. M.; Vlasov, Y. A. *Nuovo Cimento D* **1995**, *17*, 1349.
(12) Vlasov, Y. A.; Bo, X. Z.; Sturm, J. C.; Norris, D. J. *Nature* **2001**, *414*, 289.
(13) Müller, M.; Zentel, R.; Maka, T.; Romanov, S. G.; Sotomayor Torres, C. M. *Chem. Mater.* **2000**, *12*, 2508.
(14) Jiang, P.; Ostojic, G. N.; Narat, R.; Mittleman, D. M.; Colvin, V. L. *Adv. Mater.* **2001**, *13*, 389.
(15) Egen, M.; Voss, R.; Griesebock, B.; Zentel, R.; Romanov, S. G.; Sotomayor Torres, C. M. *Chem. Mater.* **2003**, *15*, 3786.
(16) Ferrand, P.; Egen, M.; Griesbock, B.; Ahopelto, J.; Müller, M.; Zentel, R.; Romanov, S. G.; Sotomayor Torres, C. M. *Appl. Phys. Lett.* **2002**, *81*, 2689.
(17) Ye, Y. H.; Badilescu, S.; Truong, V. V.; Rochon, P.; Natasohn, A. *Appl. Phys. Lett.* **2001**, *79*, 872.
(18) Yang, S. M.; Ozin, G. A. *Chem. Commun.* **2000**, 2507. Ozin, G. A.; Yang, S. M. *Adv. Funct. Mater.* **2001**, *14*, 605. Yang, S. M.; Miguez, H.; Ozin, G. A. *Adv. Funct. Mater.* **2002**, *12*, 425. Miguez, H.; Yang, S. M.; Ozin, G. A. *Appl. Phys. Lett.* **2002**, *81*, 2493.
(19) Yin, Y.; Xia, Y. *Adv. Mater.* **2002**, *14*, 605.
(20) Kumacheva, E.; Golding, R. K.; Allard, M.; Sargent, E. H. *Adv. Mater.* **2002**, *14*, 221.

10.1021/cm048834u CCC: $27.50
Published on Web 11/16/2004

Scheme 1



the possibility of E-beam processing;[4,22] this is not possible for polystyrene or SiO_2 opals. With an E-beam, line and point defects can be realized, but there are two major problems of E-beam processing. The defects have to be written point by point, which costs a lot of time, and there is no possibility for a structuring in three dimensions.

An alternative method is the photoprocessing of polymer opals in analogy to photoresists with photolithography.[23,24] This method makes a patterning of the whole opal at once possible. In combination with two-photon lithography, there is also the potential to pattern the opal in three dimensions. The needs for this system would be a special polymer for the monodisperse constituent colloids and a photosensitive system.

Systems for photolithography consist today mostly of an acid-sensitive polymer and a photoacid generator (PAG). Under illumination with UV-light, the PAG transfers chemically and creates protons. These protons catalyze reactions in the polymer, which transfers from a hydrophobic apolar polymer into a hydrophilic polymer, which is soluble in aqueous base.[25]

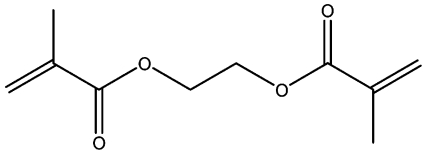
For the preparation of photosensitive polymer opals, a suitable monomer is poly *tert*-butyl-methacrylate (P*t*BMA),[26] if photoacid generators (PAGs) can be incorporated into the monodisperse colloids. As the PAGs disturb the radical polymerization, they have to be infiltrated into the preformed colloids. This requires the preparation of cross-linked colloids[12] and a swelling and deswelling of the colloids (Scheme 1).

Here, we describe the preparation of cross-linked monodisperse colloids from P*t*BMA, their filling with a suitable PAG, their crystallization into polymer opals, the chemical proof of the photoprocessing, and the patterning of polymer opals with this method.

Results and Discussion

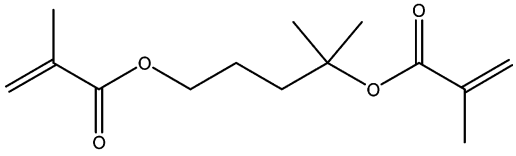
Synthesis of Photoprocessable Opals. For the following experiments, a suitable monomer is *tert*-butyl-methacrylate (*t*BMA), because the *tert*-butyl ester group can be readily cleaved under acidic conditions, yielding the acid and isobutene as a volatile side product. Because the polymer should be swellable in organic solvent, to incorporate the PAG, it must be cross-linked. In accord with earlier experiments,[26] ethylene glycol dimethacrylate **EGDMA** was used. To enhance photoprocessability, a second cross-linking agent, 4-methyl-4-methacryloxy-pentyl methacrylate **MMPM**, was synthesized. This cross-linking agent can be cleaved under acidic conditions, yielding a carboxylic acid and 4-methyl-pent-4-enyl methacrylate. A cross-linking ratio of 5 mol % was adjusted. "Surfactant-free emulsion polymerization" (SFEP) was the chosen method because it leads to a monodisperse emulsion of P*t*BMA beads in water (10 vol %). By changing the monomer−water ratio, the size of the beads can be varied; it is possible to predict the resulting beads size within a range of 20 nm.[27] The bead diameter was calculated for crystallized films (opals) with a modified Bragg equation from absorption measurements in the UV−vis range.

Formula 1:



EGDMA

Formula 2:



MMPM

Because the material should combine the properties of forming a photonic crystal and photosensitivity, a photoacid generator (PAG) and a sensitizer **Dye 1** have to be incorporated into the polymer bead structure. This is possible by diffusing the PAG and the sensitizer into polymer beads swollen in an acetone−water (2:1) mixture. First experiments with ionic PAG were not successful as the swollen colloids coagulated and precipitated after addition of the positively charged PAGs. A

(21) Tétreault, N.; Agustín, M.; Míguez, H.; Rodríguez, I.; Ozin, G. A. *Adv. Mater.* **2004**, *16*, 346.
(22) Ferrand, P.; Egen, M.; Zentel, R.; et al. *Appl. Phys. Lett.* **2003**, *83*, 5289.
(23) Soane, D. S.; Martynenko, Z. *Polymers in Microelectronics − Fundamentals and Applications*; Elsevier: Amsterdam, 1989.
(24) Thompson, L. F.; Willson, C. G.; Bowden, M. J. *Introduction to Microlithography*, 2nd ed.; American Chemical Society: Washington, DC, 1994.
(25) Dhal, P. K.; Horner, M. G.; Ingwall, R. T.; Kolb, E. S.; Mehta, P. K.; Minns, R. A.; Schild, H. G.; Waldmann, D. A. U.S. Patent 5, 1998; Vol. 759, p 721.
(26) Egen, M.; Zentel, R. *Chem. Mater.* **2002**, *14*, 2176.
(27) Egen, M.; Zentel, R. *Macromol. Chem. Phys.* **2004**, *205*, 1479.

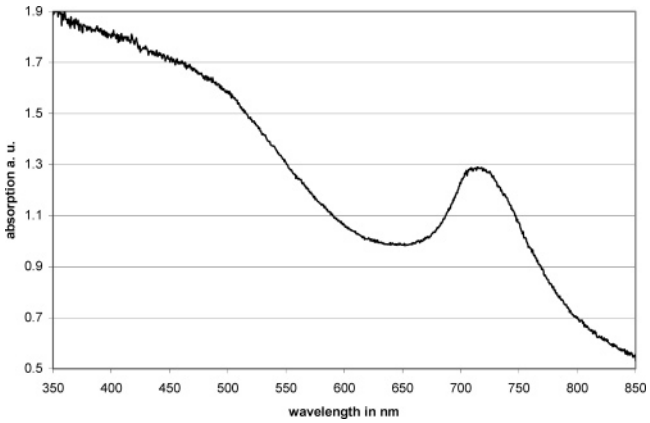
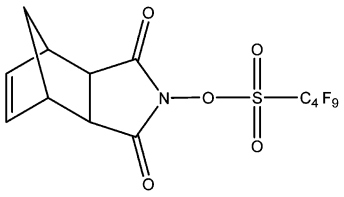


Figure 1. UV−vis spectrum of an opal (BL 6); the reflection maximum is at the wavelength 747 nm.

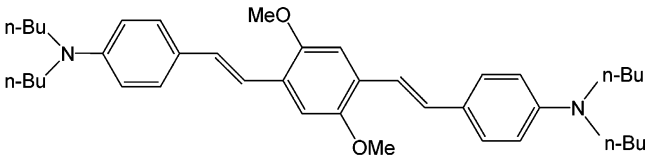
problem is that the polymer beads are negatively charged on the surface and are stabilized by electrostatic repulsion. Therefore, the positively charged PAGs neutralize the negative charges and the beads coagulate. Alternatively, a nonionic **PAG 1** was adopted, and after diffusion no coagulation occurred. After deswelling, it was possible to cast opaline films from the colloids with the incorporated **PAG 1** and **Dye 1** (Scheme 1).

Formula 3:



PAG 1

Formula 4:



Dye 1

Thin films can be casted on different substrates (glass, silicon, polymers), which have been cleaned and made hydrophilic. Usually the colloids crystallize best on glass (presumably because of the most hydrophilic surface). However, the adhesion of the opaline films to glass is poor. Therefore, the unexposed opaline film floats off, sometimes, during development with aqueous base. Opaline films on substrates such as PMMA or polycarbonate have a better adhesion and withstand a longer treatment with aqueous base. For a typical opaline film, two small droplets from a 10 vol % P*t*BMA solution in water were deposited as a thin film on the substrate. For slow drying, the films were covered in a Petri dish. The beads form a uniform opal structure during drying and therefore have photonic crystal properties. The optical properties of resulting opaline films are presented in Figure 1. In addition, the beads are photosensitive, so that they can be further patterned with light (Scheme 1).

Table 1. Collection of the Synthesized Opals from PAG-Containing Colloids[a]

sample	cross-link agent	λ_{max} (nm)	*d* (nm)	color
BL 1	EGDMA	510	233	blue
BL 2	EGDMA	560	256	green
BL 3	EGDMA	587	268	yellow
BL 4	EGDMA	606	276	red
BL 5	MMPM	670	306	red-violet
BL 6	EGDMA	717	328	violet
BL 7	EGDMA	747	340	violet

[a] The diameter of the colloids was determined from the wavelength of reflection. The colloids were cross-linked with ethylene glycol dimethacrylate **EGDMA** and 4-methyl-4-methacryloxypentyl methacrylate **MMPM**.

The different samples resulting from the crystallization of beads of a different diameter are collected in Table 1.

Patterning of Polymer Opals. The patterning of the polymer opals can be accomplished by irradiation with UV-light in the region around the absorption maximum of the PAG (210 nm) or at the wavelength of the sensitizing dye (400−450 nm). The films were exposed through a quartz glass mask. During exposure, the PAG forms acid (protons) in the irradiated area. When the polymer is annealed, the acid catalyzes an ester cleavage and the monomer units of the polymer are changed from *t*BMA to methacrylic acid and isobutene is released (Scheme 1). The chemical reaction resulting from the irradiation of the PAG can be proven by IR-measurement. The interesting part of the spectrum is the region around 1750 nm, because the carbonyl bond is in this region and there is a recognizable change in the wavelength for the different types of carbonyl bonds involved in this reaction (Figure 2). The beads that contain MA are slightly smaller (20−40 nm in diameter, volume loss of isobutene), as shown by UV−vis measurement.[26] EM measurements (see Figure 3b,c) show the decrease of diameter directly. In addition, they show that cracks in the opaline films get much wider, because of the volume shrinkage. This can be seen especially clear on a sample with a very high number of cracks (Figure 3a). While this widening of the cracks would be disastrous for photonic applications, it is not important for the patterning, because the modified beads and the cracks within their area are dissolved during patterning, leaving a blank surface.

The behavior of P*t*BMA and poly(methacrylic acid) differs strongly during exposure to aqueous base. P*t*-BMA is rather hydrophobic, and hardly wets, whereas poly(methacrylic acid) gets converted to the acid salt and dissolves in water. So with an aqueous base it is possible to selectively wash off the exposed area, which consists of the poly(methacrylic acid). The process for the spheres cross-linked with **EGDMA** is probably some kind of swelling and dissolving, because the polymer colloids are still cross-linked and thus not completely soluble. The new cross-linking agent **MMPM** advances the dissolution process, because the cross-linking agent is cleaved during exposure and heating. The unexposed area is not soluble and remains unchanged during development. So with a mask it is possible to form a two-dimensional pattern (Figure 4) in the photonic crystal.

With this method, it is possible to create defects inside a photonic crystal structure. With light, a chemical

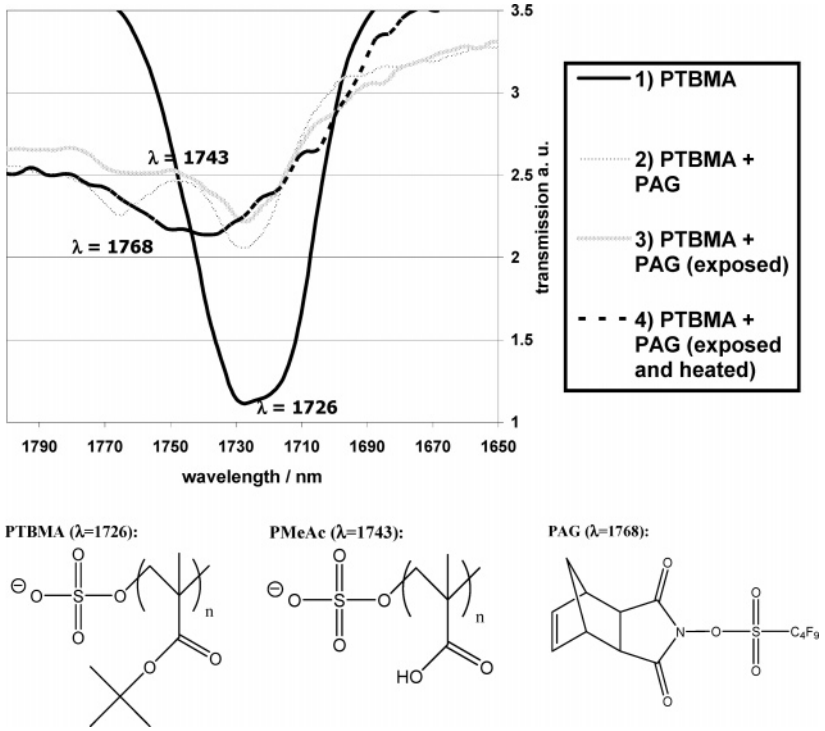


Figure 2. Line 1 shows the carbonyl bond of the untreated colloids. After swelling, a second peak for the carbonyl bond of the photoacid generator appears (line 2). This demonstrates that the infiltration was successful. After exposure, the carbonyl bond of the PAG almost disappears, presumably because the PAG decomposes and thereby generates protons. The polymer peak still remains unchanged. When the exposed polymer is heated, an acid-catalyzed ester cleavage on the polymer takes place and the carbonyl peak changes due to transformation from ester to acid in the polymer backbone (line 4); the peak of the PAG also disappears completely due to thermal destruction of the PAG.

reaction can be induced, and this reaction leads to a change in the polymer backbone. The modified backbone is polar and soluble in an aqueous base. With a mask defined, defects can be produced (Figure 5). The resolution of the defect structures is presently under investigation. It should be comparable to the resolution possible in UV-lithography.

Opals from photoprocessable colloids offer the possibility to use self-assembly for the creation of a large-scale periodic structure and UV-light for the creation of single defects. It may be advantageous in comparison to holography, with which single defects in a periodic structure are difficult to obtain, and to two-photon lithography, which requires the writing of each individual line; however, in the fabrication of 3D photonic crystals, two-photon lithography offers an attractive method to introduce defects with 3D control.

Experimental Section

Polymerization of *t*BMA. The colloid particles from cross-linked P*t*BMA were synthesized in a 250 mL flask with a nitrogen inlet, a condenser, and a mechanical stirrer according to ref 27. First, 7.55 mL of *t*BMA and 0.55 mL (5 mol %) of EGBMA in 150 mL of Millipore water were heated to 90 °C and flushed with nitrogen for 30 min. Next, 500 mg of potassium persulfate was dissolved in 5 mL of water at 90 °C under nitrogen in a 10 mL flask. After 20 min, the potassium persulfate was added to the monomers, and polymerization started. After 60 min of polymerization, the flask was opened (oxygen) to stop the polymerization and the remaining monomer evaporated. The colloids were purified from large agglomerations by filtration through a standard paper filter, followed by centrifugation.

Synthesis of MMPM. First, 0.1 mol of methylmagnesium bromide in 100 mL of dry diethyl ether was stirred in a 250 mL flask. Over 2 h, 0.033 mol of butyrolactone in 33 mL of diethyl ether was added dropwise at room temperature. The mixture was heated for 2 h under reflux. Ice and a saturated ammonium chloride solution were added until two clear phases were obtained. The ethereal phase was separated. The water phase was perforated for 48 h. The ethereal phases were combined and dried over sodium sulfate. The solvent was removed in a vacuum. A fractionated distillation of the residue gave 2.771 g (70.4% yield) of a colorless viscous liquid of 2-methyl-2,5-pentandiol (boiling point 75 °C at 6×10^{-3} mbar). Next, 22.9 mmol of diol, 73.3 mmol of pyridine, and 40 mL of dichloromethane were stirred under nitrogen in a 100 mL flask at 0 °C. Methacryloyl choride (68.7 mmol) was then added, and the mixture was stirred at 0 °C for 2 h. The mixture was stirred overnight at room temperature. The mixture was shaken three times with 30 mL of water. The organic phase was dried with sodium sulfate. The solvent was removed, and the product was cleaned with a column (PE:EE:triethylamine, 100:19:1).

Diffusion of PAGs/Dyes in PtBMA Colloidals. In a vial were dissolved 25 mg of PAG 1 and 1 mg of **Dye 1** in 1 mL of acetone, and they were mixed with 0.5 mL of P*t*BMA emulsion in water (10 vol %). For diffusion, the mixture was stirred overnight. For fast shrinking, the mixture was poured into 10 mL of ice water and was filtered afterward. After centrifugation, a concentrated dispersion of PAG and sensitizer containing beads in water was obtained.

Preparation of Substrates and Crystallization. Glass and silicon were cleaned by etching for half an hour with 7 M sodium hydroxide solution. PMMA and polycarbonate substrates were cleaned in an oxygen plasma for 2 min at 50 W. From a 10 vol % P*t*BMA solution in water, two small droplets were deposited as a thin film on the substrate. For slow drying, the films were put under a Petri dish. The drying took about 12 h.

Exposure Method. The films were exposed with a strong UV-lamp (Oriel Instruments 68910 Arc Lamp Powersupply

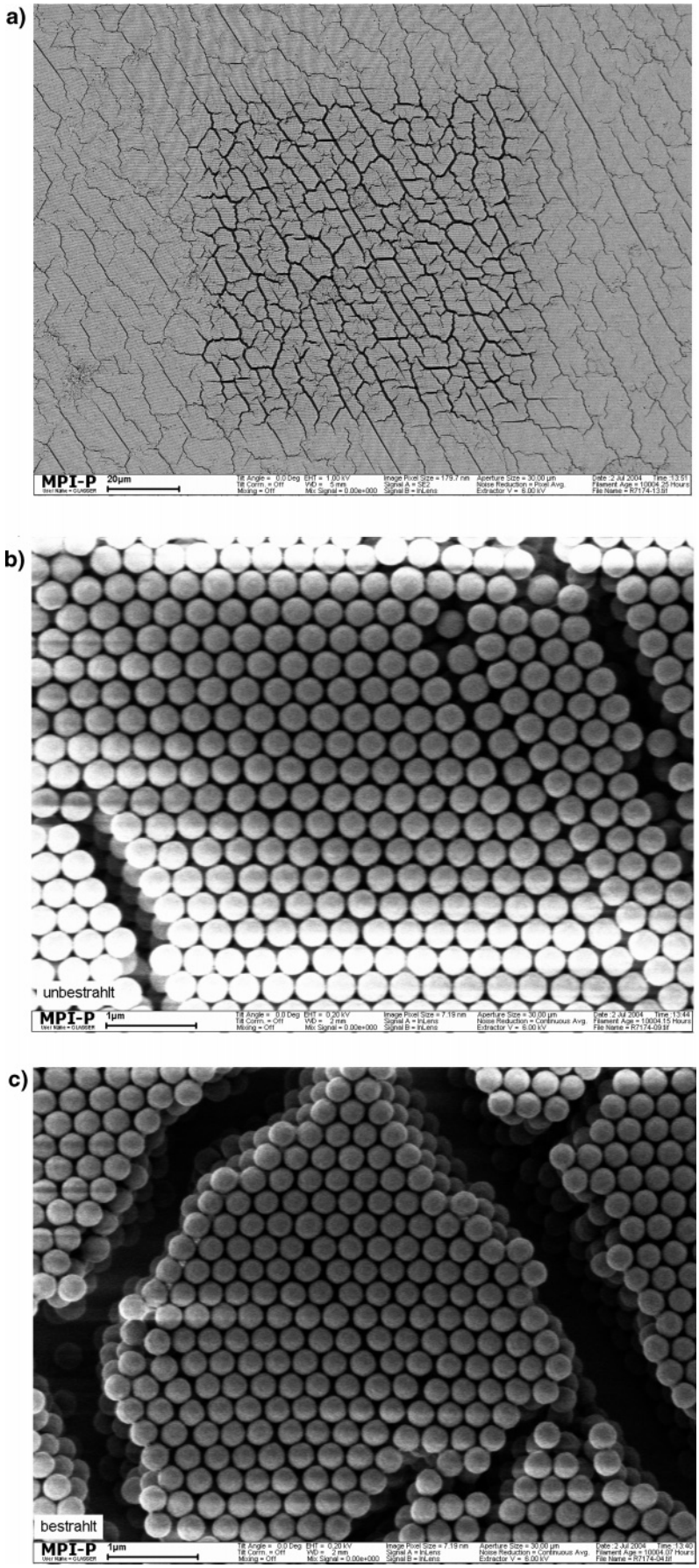


Figure 3. These SEM pictures show an opaline film of BL 6. (a) An overview of an exposed square surrounded by unexposed region is shown. It can be observed that the cracks in the exposed area are a lot wider, because of the volume shrinkage. (b) A magnification of the unexposed area; the bead diameter is 330 nm. (c) Here, the exposed region is aggrandized; the bead diameter is 290 nm.

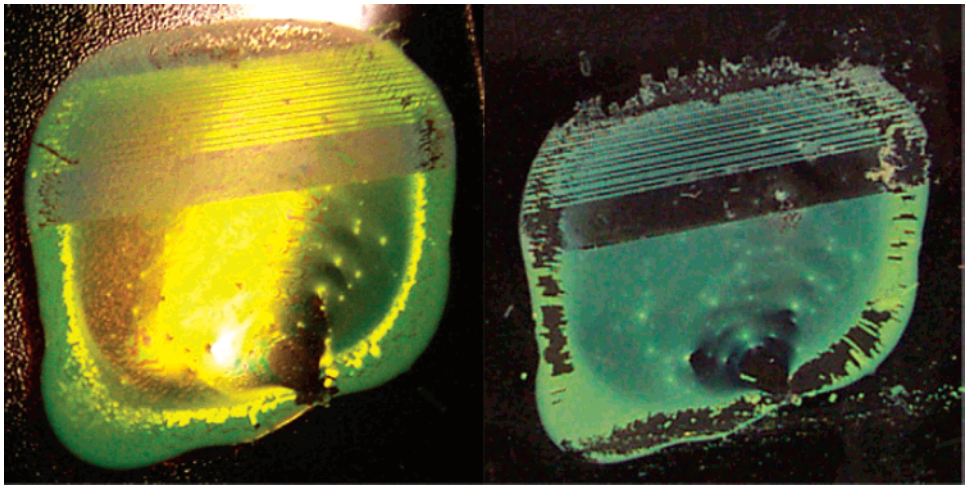


Figure 4. A picture of an opaline film from BL 2. On the left side, an exposed film is shown. The bright colored area is unexposed; the exposed area is not so bright for the current incidence of light, because of the smaller bead size. On the right side, the same film is shown after developing. The exposed area is dissolved in the developer; the unexposed area remained on the substrate.

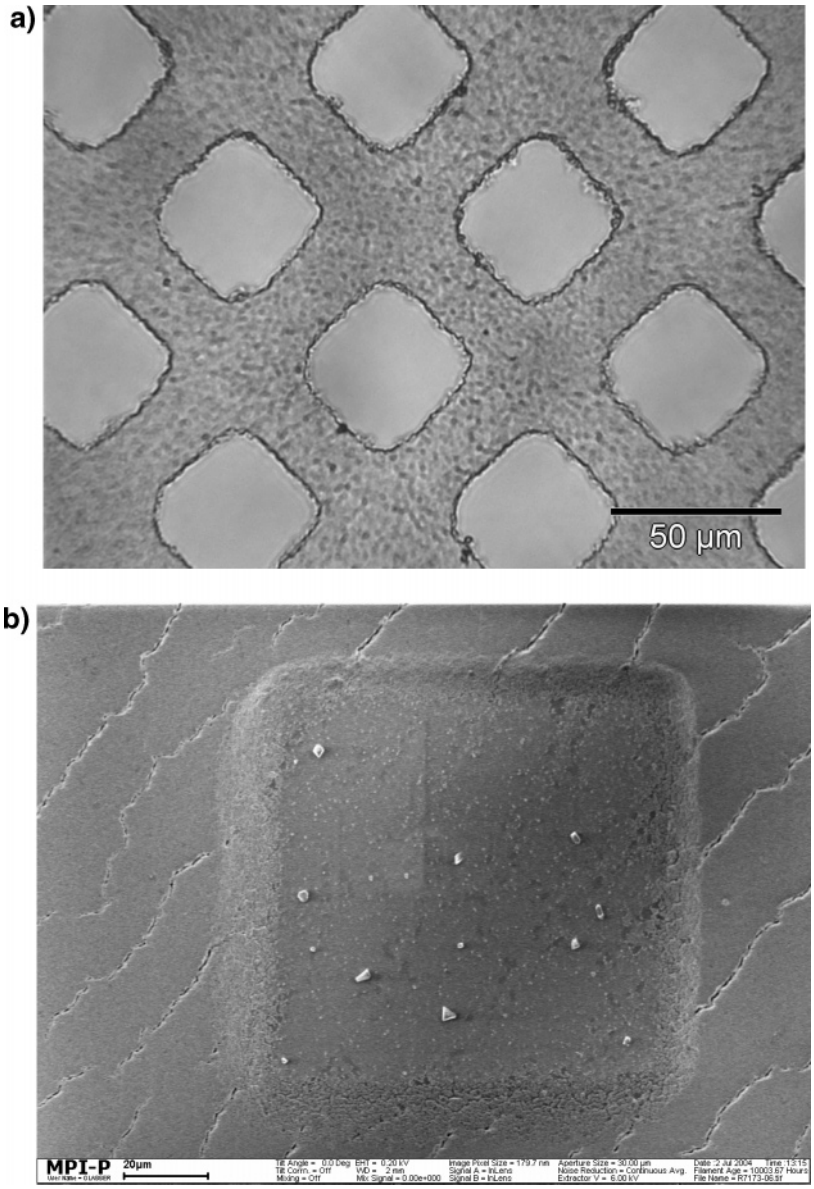


Figure 5. (a) Optical microscopy of patterned photonic crystal films. The dark areas represent the unchanged photonic crystal film; the bright areas represent the clean substrate. (b) SEM picture of a single square. In the center of the picture, there is the developed region, and one can see the clear substrate. The outer region is the unchanged polymer opal.

500 W Hg) using a filter (280−400 nm). Time (0.5−10 min) and distances (5−20 cm) were varied.

Development Method. After exposure, the films were heated at 120 °C for 10 min. The films were then developed in an aqueous sodium carbonate solution (10 wt %) for 30 s, cleaned with distilled water, and dried.

Used Chemicals. The lattices and the cross-link agent were synthesized using commercially available chemicals without further purification: Ethylenglycolbismethacrylate (EGBMA) [Acros], *tert*-butyl-methacrylate (*t*BMA) [Acros], potassium persulfate [Fluka], methacryloyl choride [Acros], methylmagnesium bromide [Aldrich], butyrolactone [Fluka], and PAG (CAS 307531-76-6) [Aldrich].

The dye was made at Arizona University in the group of S. Marder; the synthesis is to be published.

Acknowledgment. Financial support by the DFG (Priority program: Photonic crystals) is gratefully acknowledged. Additional support from the National Science Foundation NIRT and STC program is also acknowledged. We thank G. Glaser from the MPI for Polymer Research in Mainz for SEM measurements.

CM048834U