

# Dye-Containing Polymer Beads as Photonic Crystals

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Monodisperse PMMA beads of a size varying between 200 and 400 nm have been prepared by a modified emulsion polymerization technique. These beads sediment well on substrates to form 3-dimensional face-centered cubic packages. This method allows it to cover large glass substrates (area up to 10 × 10 cm) with an opalescent layer of the beads thus creating films with opaline structure, which can be used as photonic crystals. Choosing PMMA as the material of the beads brings several advantages, e.g., the PMMA photonic films can be precisely patterned by e-beam lithography with the feature resolution down to one bead in width and various fluorescent dyes can be incorporated in PMMA balls. Dye-impregnated PMMA opaline photonic films demonstrate the incomplete photonic band gap structure and related modification of dye photoluminescence spectrum.

## Introduction

Photonic crystals are of great interest both for fundamental and applied research. They are periodic dielectric structures that are designed to control the propagation of electromagnetic (EM) waves by defining allowed and forbidden energy bands in the photon dispersion spectrum. The absence of propagating EM modes inside the structures gives rise to distinct optical phenomena such as inhibition of spontaneous emission (for an overview, see refs 1–6). Application prospects of photonic crystals demand a search for effective and low-cost technologies which are applicable for mass production of high-quality materials. Besides, an effective design of light emitting devices based on photonic crystals requires the fabrication of 3-dimensional photonic band gap (PBG) structures incorporating the light sources with an emission band centered at appropriate frequency. An important example of a 3-dimensional photonic crystal in the visible frequency range is artificial opal.<sup>7</sup> Opal is a cubic closest packing of silica balls whose diameters are of several hundred nanometers. The photonic band gap structure of opals themselves is pronounced enough to modify the fluorescence of dyes embedded in their inner space.<sup>8,9</sup> While opals are not able to show a complete photonic band gap due

to the insufficient difference in the refractive index between the silica balls and the air they can be used as templates for preparation of inverted opaline structures from materials of high index of refraction. With certain technologies in mind the polymer-based analogies of opals, e.g., colloidal crystals based on polystyrene, have several advantages over silica opals:<sup>10</sup> (i) a modified emulsion polymerization technique used for their synthesis is comparatively easier than the Stober process,<sup>11</sup> (ii) polymers allow the incorporation of fluorescent dyes directly into the beads, (iii) the organic template can be easily either dissolved or burned away from the structure after infilling with inorganic materials.<sup>12–15</sup>

Here we report photonic crystals prepared from PMMA beads which may or may not include fluorescent dyes. PMMA used for bead synthesis is more polar as compared with polystyrene and thus a better solvent for the fluorescent dyes. This photonic crystals show an incomplete PBG and a clear influence on the emission of these dyes. Incorporation of dye molecules in PMMA balls can be performed much easier as compared with the similar procedure used in the case of silica balls where balls were first impregnated with Rhodamin and then coated with an additional silica shell.<sup>5</sup> Besides, in this work the colloidal crystal stays in a liquid and was not dried; correspondingly the RI contrast was very low. In most of the similar works reported to date the fluorescent dyes have been introduced not in balls but in polymers, which substitutes air in interstitial voids;<sup>8,9</sup>

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consequently, the refractive index contrast in such impregnated systems appears much lower than in our PMMA opaline films.

PMMA also has the advantage of being a well-known e-beam resist thus enabling to pattern the photonic crystal after sedimentation. Patterning of PMMA opaline structures is important for device applications of these structures, e.g., for wave guiding.

Following the general rule that the quality of opaline package can be improved by increasing the aspect ratio, that is the ratio of the area to the thickness, we selected the PMMA opal in the thin film form as a core of the fabrication routine. Our approach toward PMMA opaline films is free from complications involved in methods reported for thin film sedimentation so far.<sup>16–18</sup> Nevertheless, these films consist of well-ordered packages of beads, the quality of which competes with the quality of the best opaline structures.

### Experimental Section

**Preparation of the PMMA Beads (with and without Fluorescent Dyes).** In a 250 mL flask sealed by a septum, 140 mL water (and 1–5 mg of a fluorescent dye, if appropriate) were stirred for 45 min under a moderate flow of nitrogen. After the addition of 15 mL of methyl methacrylate and 15 mL of toluene, the nitrogen flow was stopped, and the suspension was tempered for 60 min at 90 °C. A solution of 500 mg of potassium peroxydisulfate in 5 mL of water (tempered for 15 min under nitrogen) was added as initiator. The polymerization was carried out under vehement stirring (1200 rpm). To stop the polymerization the flask was opened (the oxygen in air inhibits further polymerization). The toluene and remaining monomer were separated by evaporating at 90 °C under a flow of air. Particles of larger sizes were separated by filtration and centrifugation (5 min at 5000 rpm). To remove ionic impurities the beads were separated by centrifugation (60–120 min at 5000 rpm) and redispersed in 70 mL of deionized water. The procedure was repeated four times.

**Preparation of Films.** To prepare thin films, a few drops of the emulsion was spread on microscope slides and dried at room temperature and normal pressure. The slides previously had been hydrophilized by etching for 1 h with a sodium hydroxide solution (30 wt %). SEM images of the films show about 10–50 layers of the beads.

**Determination of the Size of the Beads.** The diameters ( $d$ ) of the beads were determined directly from SEM images. It is also possible to determine the size by applying the Bragg equation to the values of the UV/vis maxima of the (111) plane

$$\lambda_{(111)} = n_{\text{eff}} \times 1.632 \times d$$

where the effective refractive index is given by  $n_{\text{eff}} = fn_{\text{PMMA}} + (1 - f)n_{\text{air}}$ , the refractive index of poly-methyl methacrylate<sup>19</sup> is given by  $n_{\text{PMMA}} = 1.4893$ ,  $n_{\text{air}} = 1$ , and the filling factor for ideal face-centered cubic packing is  $f = 0.74$ .

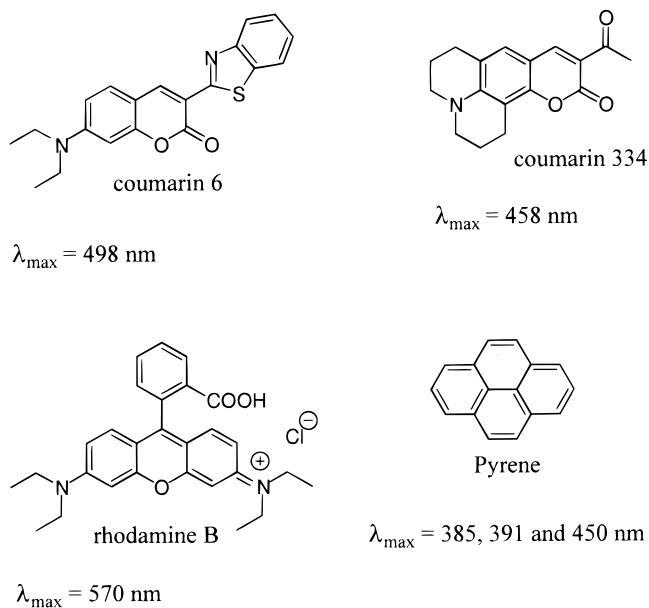
The results are summarized in Table 1.

**Patterning by Electron Beam Writing.** An electron microscope equipped with an electron beam writer (Philips XL 30 SFEG) was used to create the pattern on a polymeric opal film. The exposure was carried out with an applied voltage of 20 kV, a current intensity of 15 pA, and a stepwidth of 15 nm. To develop the film, it was dipped for 30 s into a mixture of

**Table 1. Bragg Peaks and Diameters of PMMA Beads**

no.	$\lambda_{(111)}$	$d_{(\text{Bragg})}/\text{nm}$	$d_{(\text{SEM})}/\text{nm}$	incorporated dye
b1	466	210		pyrene
b2	496	223	216	coumarin 334
b3	548	246		coumarin 6
b4	551	248	242	coumarin 334
b5	559	251	252	
b6	610	274	269	coumarin 334
b7	619	278	279	rhodamine B
b8	640	288	289	
b9	799	359	372	
b10	900	405	410	

**Scheme 1. Fluorescent Dyes and Their Maxima of Fluorescence (solvent, PMMA films)**



2-propanol (75 vol %) and 4-methyl-2-pentanone (25 vol %). After washing with 2-propanol, the film was dried in a nitrogen flow.

**Instrumental Details.** Electron microscopy was carried using a Philips XL 30 SFEG electron microscope. UV/vis transmission spectra were recorded on a Shimadzu UV-2102 PC spectrometer. To record the angle-dependent reflection spectra, a 250 W halogen lamp and an ISA 270 M spectroradiometer were used. The photoluminescence spectra were recorded using a Spectra Physics Beam Lock 2080 Laser (Ar<sup>+</sup>, 20 W) and a SPEX 1680 double spectrometer.

### Results and Discussion

#### Preparation of the PMMA Opaline Structures.

The monodisperse PMMA beads of a size varying between 200 and 400 nm were prepared by a modified-emulsifier free-emulsion polymerization technique<sup>20</sup> (see Experimental Section). Different laser dyes have been incorporated in PMMA beads during the bead synthesis by adding them to the polymerization batch. Scheme 1 lists their chemical structure together with their maxima of fluorescence.

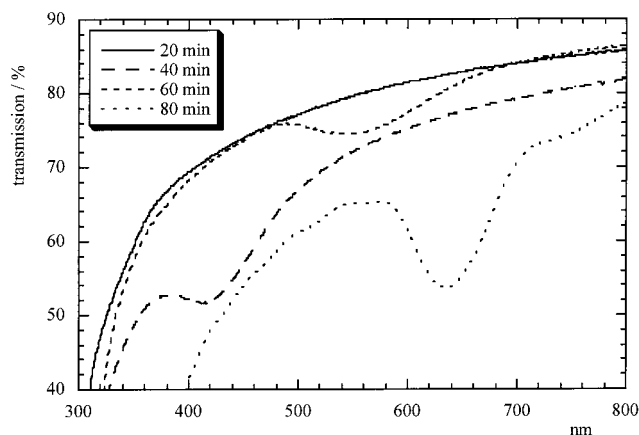
The latex obtained in this way is stabilized only by the few sulfate groups originating from the decomposition of the initiator (peroxydisulfate). The size of the PMMA beads depends strongly on the reaction time. At high turnovers the resulting crystals show Bragg reflection.

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**Figure 1.** Transmission spectra showing a bathochromic shift of the Bragg peak (dried latex films) and thereby the growing of the size of the beads.

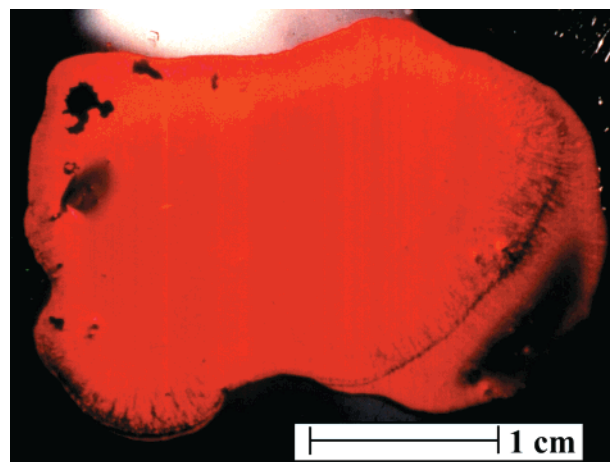
tion in the near-infrared. To control of the diameters of the beads the polymerization must be stopped at the right time. Particularly in order to obtain the interference color in the visible part of the spectrum the required polymerization time is between 20 and 40 min. The monitoring of the bead growth was made by probing the polymerizing mixtures at 5–10 min intervals and drying them on hydrophilized microscope slides. Figure 1 shows the alteration of transmission of test samples with polymerization time. The minimum on these spectra corresponds to the optical stop band of the photonic crystal, and it appears at spectral position satisfying the conditions of the Bragg resonance.

To vary the diameters of the beads toluene was added to the reaction batch. Toluene swells the beads first but evaporates later leaving smaller beads. Since a higher dilution of the monomer leads not only to smaller beads but also to lower yields, a 1:1 ratio of MMA and toluene was used as compromise. Typical sizes of the PMMA beads, as determined for the dried latex, are collected in Table 1.

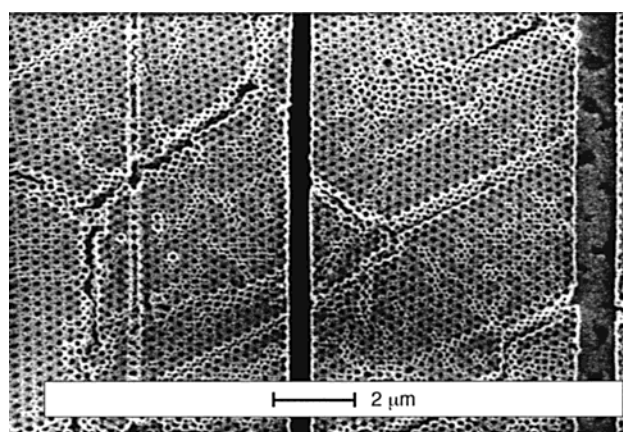
The dispersions of PMMA beads sediment well on substrates, leaving, after drying at room temperature (below  $T_g = 105\text{ }^\circ\text{C}$ ), a dense packing of balls. Thin films from PMMA beads were prepared by dropping a small amount of the emulsion on microscope slides or silicon substrates and subsequent drying at room temperature and normal pressure. It is possible to cover large glass plates up to  $10 \times 10\text{ cm}^2$  area with an opalescent layer of the beads by this simple procedure. Drying in an atmosphere with constant humidity (98%) during 2 days allows preparing thicker more perfectly packed films with brighter reflection colors (see Figure 2). Scanning electron microscopy (SEM) shows films consisting of about 10–100 layers of the beads.

Electron microscope equipped with an electron beam writer was used to pattern the polymeric opal film. To develop the film it was dipped into a mixture of 2-propanol and 4-methyl-2-pentanone. Figure 3 shows the SEM image of the thin film of the beads (about 10 layers thick) on a glass plate. The test pattern in the form of straight lines with a width of about 1, 3, or 5 beads have been written with an e-beam for the full depth of this film.

**Determination of the Size of the Beads.** The diameters ( $d$ ) of the beads were determined directly



**Figure 2.** Optical impression of a thin film photonic crystal from PMMA beads (b8, Table 1).



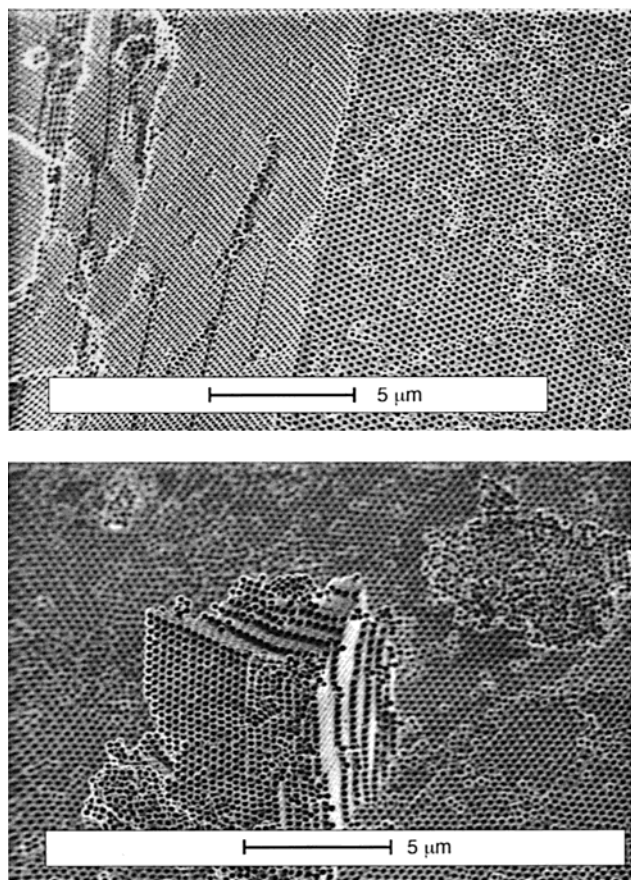
**Figure 3.** SEM image of lines written on a film of PMMA beads by e-beam writing.

from SEM images. They are collected in Table 1. SEM was operated at low accelerating voltage that allows observation of the structure without coating with a conductive metal layer. A nearly perfect packing of the 200–400 nm large beads (see Figure 4) has been observed. Samples dried slowly at high humidity (see Figure 4a) with a thickness of about 10–100 layers show a nearly perfect packing throughout the thin film. Thicker samples (up to about  $50\text{ }\mu\text{m}$ ) can be crystallized well. As an extreme case samples of up to several millimeters thickness have been prepared by centrifugation. They show a perfect packing at the surface and the interface with the glass wall (see Figure 4b). This orientation is, however, lost in depth from surface into the bulk sample where only a short-range order remains.

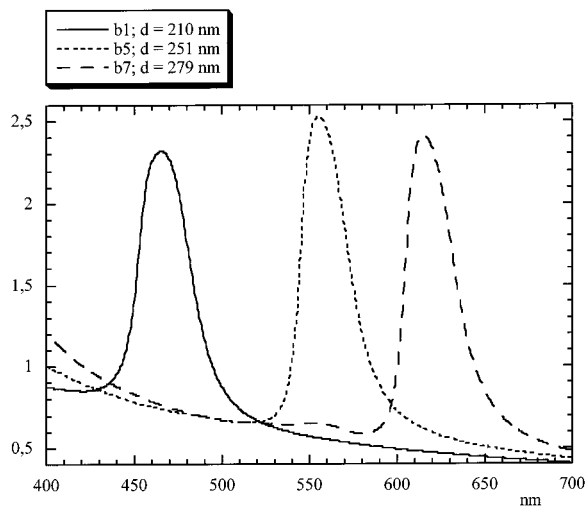
Alternatively the size of beads was determined by applying the Bragg equation to the values of the diffraction maxima from the (111) planes of the bead package. Both values agree well. They are summarized in Table 1.

**Optical Properties.** Spectra of scattered light show the optical stop-bands associated with the 3-dimensional structure of PMMA opaline films (Figure 5). The enhancement of the scattered light appears at the frequency range of the Bragg resonance. This resonance comes from the diffraction of the incident light on the set of (111) planes in the face-centered cubic package





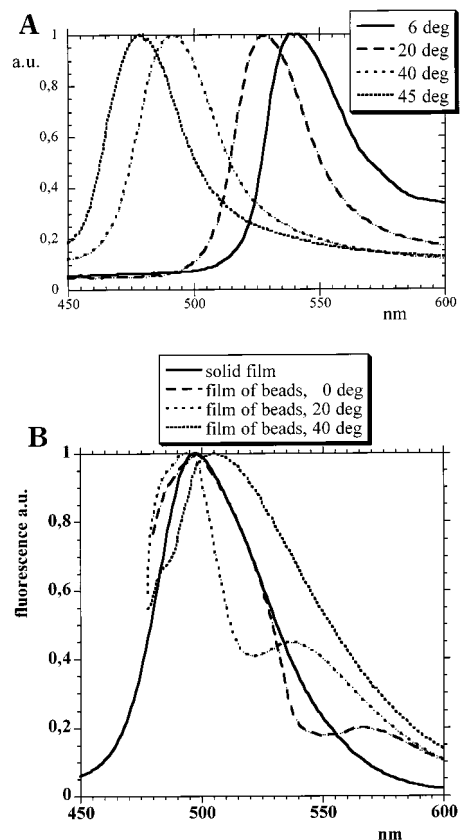
**Figure 4.** SEM image of (top) a sample dried slowly at high humidity (about 50  $\mu\text{m}$  thick, the image shows a fracture edge) and (bottom) a thick sample (several mm) prepared by centrifugation.



**Figure 5.** Reflectance spectra of films prepared from PMMA beads of different diameters ( $d$ ). The UV/vis spectra are not influenced by absorptions of incorporated dyes. In the spectrum of b7 rhodamine B causes only a very weak band at about 550 nm.

of beads. It was observed at wavelengths ranging from 400 to 800 nm (see Figure 5 and Table 1) depending on the bead size.

Optical reflectance spectra collected from an illuminated spot of about 1  $\text{cm}^2$  give evidence of the good ordering of the bead package over the large area. The intensity of the scattered light at the maximum of the



**Figure 6.** (a) Normalized reflection spectra showing the angle dependence of the Bragg peak. The beads (b3) of the corresponding film have diameters of 246 nm and contain the fluorescence dye coumarin 6. (b) Normalized photoluminescence spectra recorded from the same film as the spectra of a.

Bragg resonance is about 20 times larger than the intensity at the background. This value is comparable to the characteristics of the best opals reported so far. Direct comparison of the optical quality of bulk and thin film opals is not possible, because of the difference in the regime of the light propagation in the thin opaline film and bulky opal slabs. The relative bandwidth of the Bragg resonance (ratio of its full bandwidth taken at the half-height of the peak to the central frequency of this resonance) is about 5%. That correlates fairly well with the theoretical calculations of the bandwidth of the scattering resonance for the perfect face-centered cubic lattice of balls with refractive index of 1.5 in air.<sup>21</sup> The confirmation of the uniformity of the PMMA opaline film is the observation of Fabry-Perot oscillations around the Bragg resonance reported for the first time.<sup>22</sup> It is associated with the reflection of the light at the upper and bottom surfaces of the film. Obviously, these oscillations would be washed out for films of nonuniform thickness.

The angular dependence of the Bragg resonance for the PMMA film consisting of beads filled with coumarin 6 (b3 from Table 1) is given in Figure 6a. With increasing angle between the normal to the film surface and the light beam the reflection resonance shifts to shorter wavelengths. There is no overlap of particular

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resonances despite the large variation of the angle of the incident light. The meaning of this angular dependence is the demonstration of the rate of incompleteness of the PBG structure.

It is one of the interests in photonic crystals to modify the emission of light (fluorescence) by the superstructure. For this purpose different fluorescent dyes (see Scheme 1) have been incorporated into the polymer beads. The size of the beads (Table 1) has been selected in such way that the fluorescence wavelength (see Scheme 1) is a bit shorter than the Bragg resonance at normal incidence. This allows the investigation of the effect of the photonic band gap structure on the photoluminescence spectra. Figure 6b demonstrates this clearly for beads filled with coumarin 6 (b3) (coumarin 334 and pyrene could not be investigated to date because the wavelength of the excitation laser is too long compared to the absorption wavelength). Light emitted in the frequency range of the scattering resonance (Figure 6a) cannot propagate through the photonic crystal in certain directions and becomes partially localized in the vicinity of dye molecules. Due to the enhanced reabsorption of the emitted radiation, the excited dye molecules are forced to relax nonradiatively. This effect is seen as a decrease of the emission intensity in the spectral range of the photonic band gap (Figure 6b). The angular variation of the emission minimum corresponds to that in the reflectance spectrum.

It should be pointed out that this effect should be much larger, if the fluorescent dye would be distributed only under the surface of the film of beads. In the samples investigated here, the fluorescence from the near-surface volume of the film remains unaffected by the photonic band gap structure. Consequently, this contribution reduces the total effect upon the emission spectrum.

## Conclusion

PMMA beads prepared by a modified emulsion polymerization sediment well on hydrophilic substrates. They are thus ideal candidates for the preparation of thin film photonic structures (cm<sup>2</sup>) with optical properties comparable to the best bulk opals. They have the advantage that they can be patterned as e-beam resists. In addition they are more polar than polystyrene and thus a better matrix for various fluorescent laser dyes.

The influence of the photonic structure on the emission properties of the dyes and the infilling with inorganic materials (to increase the refractive index contrast) is under current investigation.

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