Polydisperse Isomers of Poly(ethylene glycol) Methacrylates

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We report the first polydisperse isomers of poly(ethylene glycol) methacrylates by a novel convergent approach. These macromolecules can be prepared by a metalloenzyme-catalyzed polymerization of α-bromoethyl methacrylate. The product distribution is controlled by the concentration of the α-bromoethyl methacrylate monomer. The resulting polymers have a monodisperse polymerization index of about 1.5, which is significantly lower than that of the pure monomer. This method offers a convenient way of preparing polydisperse polymers with a wide range of molecular weights. The polydisperse isomers may find applications in various fields such as biomedical and pharmaceutical sciences.

**References**


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freely than in TIR guidance, because the PBG conditions depend only on the properties of the cladding stacks. Guided modes can exist with mode indices $\beta/k$ that are lower than the mean index of the stacks (the frustrated tunneling PBG case) or even lower than the lowest index of the stacks (the Bragg PBG case), conferring extra design freedom on PBG compared with TIR guidance and allowing confinement within a hollow core. To the best of our knowledge, every type of conventional low-loss 2D waveguide so far reported uses TIR as the guidance mechanism [including our own “endlessly single-mode” PCFs (6)].

PBG guidance in a fiber requires the existence of a 2D PBG over a range of $\beta$ values in whichever materials system is used. Although we achieved this with frustrated tunneling PBG guidance in our silica-air honeycomb PCF (7), it is clear (8) that an even greater breakthrough would be achieved if the fiber guided by means of a Bragg PBG, for this would permit the concentration of optical power in air. Such a “vacuum guide” would have many of the desirable features of an empty metal-clad micro-

wave channel guide, including the ability to support extremely high power densities without breakdown, and it would have the potential to push the threshold intensities for stimulated Raman and Brillouin scattering (among other nonlinear effects) up to extremely high levels.

We have shown that simple triangular lattices of air holes in silica (index contrast $1:1.46$) can have full 2D PBGs in the Bragg regime of $\beta$ values (that is, $\beta < k$) if the air-filling fraction is relatively high (3). Theory fails to predict full PBGs in silica-air honeycomb PCFs in the Bragg PBG regime, but this is perhaps not surprising because the honeycomb fiber has a higher proportion of silica and so is less likely to have PBGs at low values of $\beta/k$.

The method of fabricating an air-guiding PBG fiber follows our previously reported procedure for PCFs (5, 9). Tubes of silica glass are pulled down to capillary canes on a fiber-drawing tower. These canes typically have external diameters of the order of 1 mm. The PCF preform is constructed by stacking together by hand several hundred capillary canes to form the required crystal structure on a macroscopic scale. The entire stack is then held together while being fused and drawn down into fiber by an optical fiber-drawing tower. A typical fiber diameter is 40 to 100 $\mu$m, the total collapse ratio being of the order of $10^4$. The final fiber cladding consists of a triangular array of air holes in silica, with interstitial holes that result from stacking circular capillaries. The fraction of air in this part of the fiber needs to be relatively large for the fiber to exhibit a sufficiently broad band gap—typically more than about 30% by volume.

The fiber core was formed by including a larger air hole in the center of the preform. We have studied fibers where this larger hole had an area of one or seven unit cells of the cladding material. In each case, the hole was created by leaving out the appropriate number of canes from the center of the preform stack. The whole structure was then fused and pulled into fiber. Of the resulting fibers, those formed by omission of just a single cane did not guide modes in the air (at least not at visible wavelengths). From this point on we restrict our discussion to fibers with a seven-unit-cell air core (Fig. 2).

We carried out initial characterization by holding ~3-cm-long samples vertically, illuminating them from below with white light (using a tungsten halogen lamp), and observing the light transmitted through them in an optical microscope (Fig. 3). The central air core is filled with a single lobe of colored light, its transverse profile being smooth, peaked in the center, and falling off to very low intensities at the glass-air boundary. A significant amount of white light is present in the periodic cladding, and it appears colorless in comparison with the mode trapped in the core. Different colors of the vacuum-guided mode were seen, depending on the overall fiber size and the drawing conditions used. The precise color was sometimes hard to assign by eye, and in some cases appeared to be a mixture of different colors, for example red and blue. For appropriate excitation with the white light source, a few samples support a similarly colored two-lobed mode, which we attribute to a second guided mode falling in the same band gap as the first.

The transmission spectra through the air core of lengths of fiber were measured by linking the microscope by means of a conventional multimode fiber to an optical spectrum analyzer. The spectral dependence of the waveguiding in the air hole (Fig. 4) demonstrated that several well-defined bands of transmission are present, covering the whole visible spectrum and extending into the infrared. Within each transmission band, the losses are small (over fiber lengths of several centimeters) or zero, whereas between these bands the losses are much larger, as expected in the absence of PBG effects (10). We attribute each of these bands to a full 2D PBG. Because the pitch of the crystal is large in

Fig. 3. Optical micrograph of the field intensity pattern at the exit face of a ~3-cm-long piece of fiber for white light excitation at the entrance face. White light is in the cladding regions, and the isolated and brightly colored vacuum-guided mode is in the center. Complete removal of cladding modes is difficult because of the incoherent illumination and the relatively large air holes in the structure, but they have been much reduced in the picture (without affecting the guided mode) by the application of index-matching liquid to the sides of the fiber. The effects of chromatic dispersion of the objective lens, structural features on the flat fiber surface, and the color response of the photographic film account for other minor colored features on the fiber end-face.
comparison with the wavelength, the PBGs responsible for the guidance are of high order. By selecting lengths of fiber that had been found to guide light at appropriate wavelengths, we excited this mode using laser sources. The laser light guided in the air core formed a stable, smoothly varying, single-lobed pattern in the far field. Fibers that have maxima in their transmission spectra at a particular laser wavelength guide such laser light in the core over lengths of several tens of centimeters (corresponding to hundreds of thousands of optical wavelengths). The length is presently limited by fluctuations in the fiber parameters, which cause the wavelengths of the guided modes to vary along the length of fiber. Although the short lengths of fiber that we have available preclude systematic study of losses, we transmitted 35% of a laser beam in the guided mode over a 40-mm length of fiber. The biggest contribution to the overall losses in that experiment was the input coupling efficiency. In other fibers that do not support guided modes at the laser wavelength, laser light coupled into the fiber in exactly the same guided modes at the laser wavelength, laser losses in that experiment was the input coupling have not been found to support guided modes. The number of guided modes that a conventional fiber can support is determined by the core-cladding refractive index difference and the size of the core. This follows fundamentally from state-space arguments closely analogous to well-known density-of-states calculations in solid state physics and leads to the result that the approximate number of spatial modes in a conventional fiber is as follows (1):

$$N_{\text{core}} = \frac{k^2(n_1^2 - n_2^2)r_c^2}{4}$$

where $r_c$ is the core radius and $n_1$ and $n_2$ are the core and cladding indices. (There are of course two polarization states per spatial mode.) In a hollow-core PCF, a similar expression may be derived for the approximate number of spatial modes present in the hollow core:

$$N_{\text{PBG}} = \frac{(\beta_1^2 - \beta_2^2)r_c^2}{4}$$

or

$$= \frac{(k^2n_1^2 - \beta_1^2)r_c^2}{4}$$

where $\beta_1$ and $\beta_2$ are the upper and lower edges of the PBG at fixed optical wavelength, and the second expression applies if the upper PBG edge extends beyond the maximum core wave vector, that is, $k^2n_1^2 < \beta_1^2$. Theory shows that, for a typical triangular array of air holes in silica, the photonic band gap width $\Delta \beta = \beta_1 - \beta_2$ is a small fraction of its average position $\beta_{\text{av}} = (\beta_1 + \beta_2)/2$. For example, with the data published in (3), at $\beta_{\text{av}} = 9$, $\Delta \beta = 0.2$, and taking $r_c = \Lambda/2$ for a single missing cane ($\Lambda$ is the interhole spacing), the expected number of spatial modes is 0.23, making it unlikely that any air-guided mode will be seen. On the other hand, if seven canes are removed, the hollow core area is increased by a factor of 7, the core radius by $\sqrt{7}$, and the expected number of spatial modes becomes 1.61, suggesting that a seven-cane hollow core will support at least a single transverse mode (two polarization states) and perhaps a second transverse mode. These predictions are consistent with our observations that fibers made with a single-cane air hole do not support air-guided modes, whereas those with a seven-cane hole guide light in one or two modes.

The potential practical advantages of a single-mode vacuum guide are myriad. It is easy to couple light into the core, because (unlike the honeycomb PBG fiber, which has a complex six-lobed modal pattern) the phase is constant across the air core (giving a Gaussian-like intensity profile). Fresnel reflections, which are a problem in fiber devices where light is extracted from a fiber and then reinserted after modulation or amplification, will be extremely small in the vacuum-guided fiber, because the refractive index discontinuity between the outside world and the fiber mode can be tiny. Another obvious advantage over other optical fibers is that the performance is much less limited by the interaction (absorptive or nonlinear) between the guided light and the normally solid material forming the fiber core. This will allow transmission of wavelengths and power levels not possible in conventional fibers, and will lead to greatly increased threshold powers for stimulated Raman, Brillouin, and color-center effects. On the other hand, if the hollow core is deliberately filled with a gas, vapor, or low-index liquid, very strong interactions are possible with the light in the guided mode. This may prove useful for gas sensing and monitoring, for the generation of multiple optical wavelengths by nonlinear processes, and more generally in enhanced nonlinear optics. The narrow-band performance of the fiber suggests that it might be useful as a spectral filtering device. The ability to form a single transverse mode in a tube of vacuum offers possibilities in the fields of atom guiding and laser delivery of small particles.

Fig. 4. Intensity spectrum of the light transmitted through the air core, plotted against normalized frequency $k\Lambda$ and wavelength $\lambda$, through a fiber excited with white light. Low-loss transmission bands, widths of about 3 frequency units, are separated by regions of much higher loss. The measurement is limited by the low spectral intensity of the white light source in the ultraviolet wavelength region (au, arbitrary units). The spectrum was recorded with a resolution of 10 nm. The relative normalized scales of the different transmission bands reflect the different coupling efficiencies to and from the guided mode at the widely varying wavelengths, and possibly the existence of a second mode in some band gaps.

References and Notes

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