

# *Trans*-4-stilbenemethanol-doped photosensitive polymer fibers and gratings

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We report the development of photosensitive polymeric optical fibers for gratings. The fiber cladding is made of a copolymer of methyl methacrylate and butyl methacrylate, and its core is made of a copolymer of methyl methacrylate, ethyl methacrylate, and benzyl methacrylate (90/4/6 molar ratio) doped with *trans*-4-stilbenemethanol. Ultraviolet absorption and photoinduced refractive-index change of the doped core system are presented, and its photosensitivity is demonstrated by fabrication of Bragg gratings in the core of the fiber by use of a pulse laser at 325 nm. © 2004 Optical Society of America

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Fiber Bragg gratings (FBGs) written in polymeric optical fibers (POFs) have several attractive features. The reflection wavelength of polymeric FBGs can be tuned over a much larger range than those of glass fibers. Polymeric FBGs are more sensitive to pressure and temperature because of the smaller Young's modulus and larger thermo-optic coefficient of polymers. Polymeric FBG sensors are good candidates for medical applications because of their good biocompatibility. A FBG written in a poly(methyl methacrylate) (PMMA) fiber was first reported in 1999 by Xiong *et al.*<sup>1</sup> The fiber used by Xiong *et al.* had a core made of a copolymer of methyl methacrylate (MMA), ethyl methacrylate (EMA), and benzyl methacrylate (BzMA), required a long period of UV irradiation, and was prone to physical damage within the fiber core.<sup>2</sup> This is not desirable because the irradiation leads to adverse effects on its physical and mechanical properties. There is thus a need to develop photosensitive POF with a high wavelength selectivity suitable for writing FBGs efficiently.

In this Letter we propose a photosensitive PMMA-based POF system that has a cladding made of a copolymer of MMA and butyl methacrylate (BMA) (90/10 molar ratio) and a core made of a *trans*-4-stilbenemethanol-doped MMA-EMA-BzMA (90/4/6 molar ratio) copolymer. *Trans*-4-stilbenemethanol is a stilbene derivative compound that exhibits a reversible *trans*-*cis* photoisomerization.<sup>3</sup> The refractive indices of these compounds are different when they take *trans* or *cis* structures.<sup>4</sup> Usually the *trans* species exhibit a higher refractive index, which provides an opportunity for the realization of photoinduced refractive-index change by photoisomerization.

The POF samples were prepared by the preform drawing technique. The preform was fabricated by use of bulk polymerization of monomers.<sup>5</sup> All monomers were purified according to the operation procedures given in our previous paper,<sup>6</sup> and the dopant, *trans*-4-stilbenemethanol (Aldrich), was used as purchased without further purification. Preforms

were first formed by bulk polymerization of monomers in a size-controlled glass tube, and the dopant was introduced to the core component before polymerization of core monomers.

Figure 1 shows UV absorption spectra of the cladding and core materials. The spectra of several 3.6- $\mu\text{m}$ -thick films spin coated on fused silica were measured with a Perkin-Elmer Lambda 18 UV/Vis spectrometer. Curve 1 depicts the spectrum of the cladding material, MMA-BMA (90/10 molar ratio) copolymer, which is nearly the same as the spectrum of PMMA. Curve 2 shows the MMA-EMA-BzMA (90/4/6 molar ratio) copolymer core material without doping with *trans*-4-stilbenemethanol. Curve 3 shows the UV absorption spectrum of the *trans*-4-stilbenemethanol-doped core material. Large absorption over a wide wavelength range around 310 nm can be observed for the *trans*-4-stilbenemethanol-doped

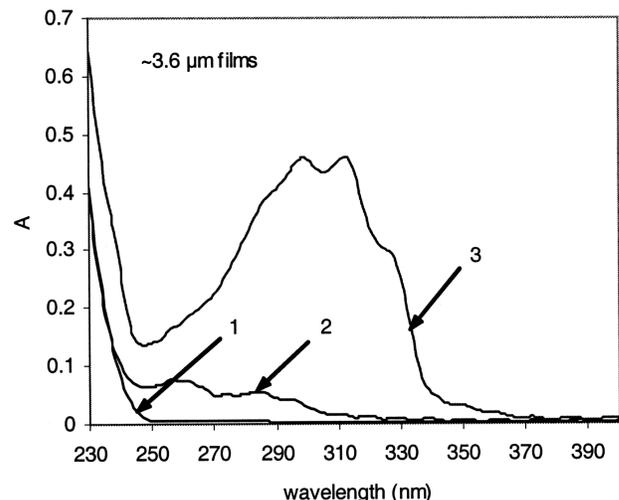


Fig. 1. UV absorption spectra of *trans*-4-stilbenemethanol-doped MMA-EMA-BzMA (90/4/6 molar ratio) copolymer core. 1, cladding MMA-BMA (90/10 molar ratio); 2, core without dopant; 3, core with 1% wt. dopant.

core material, with three absorption peaks centered at 298, 310, and 324 nm.<sup>7</sup>

The UV photoisomerization of *trans*-4-stilbenemethanol polymer films, containing 1% (in weight) of the dopant and used for the core material, were studied. In this experiment the light source was UV light generated by an UV lamp (500-W UV high-pressure mercury lamp). A narrow-bandpass optical filter was used to obtain 320-nm UV light for irradiating the films. The film samples were placed 17 cm below the UV lamp. The exposure time per pulse was fixed at 1-min duration, and prolonged exposures were composed of several 1-min pulses to avoid heating of the sample during the irradiation process. Figure 2 shows the changes in the UV spectrum after different irradiation times. A constant decrease in absorption around 310 nm was observed with increasing irradiation time. In general, *cis* isomers of stilbene and its derivatives have relatively low absorption around the peak absorption wavelength of their respective *trans* isomers; the observed continuous decrease of absorption confirms the transformation of stilbenemethanol from a *trans* to a *cis* structure. Since the core section in single-mode optical fibers is always enclosed by a thick cladding layer, we simulated this condition by placing the film made of the fiber core material beneath a thick cladding (PMMA) film ( $\sim 60 \mu\text{m}$ ). The UV spectrum change of the film behind the cladding layer was examined and compared with that without a PMMA layer shield (Fig. 3). The *trans*-4-stilbenemethanol-doped film displayed nearly the same photosensitive behavior when covered with the cladding layer. Since MMA-BMA (90/10 molar ratio) copolymer has almost the same UV absorption property as PMMA, it is believed that the shield of this cladding layer also has no influence on the photosensitive behavior of the doped core.

Figure 4 shows the photochemical transformation process of 4-stilbenemethanol from a *trans* to a *cis* structure upon UV irradiation. The isomer with *trans* structure has a higher refractive index than the *cis* isomer because of the change in molecular polarity.<sup>3</sup>

The refractive-index change of the *trans*-4-stilbenemethanol-doped film was examined by a prism coupler (Model 2010, Metricon Corporation). Free-standing films were used for the measurements. A film was divided into two parts—one was irradiated and the other was used as a control—and comparative results are listed in Table 1. The index decrease was detected in the part subjected to UV irradiation. The change in amplitude, although small in absolute value, was sufficient to form a fiber Bragg grating with a strong reflection signal.<sup>8</sup>

We examined the stability of the photoinduced isomerization of *trans*-4-stilbenemethanol in a core matrix by monitoring the UV spectrum of an UV-irradiated film sample at a high temperature of 80 °C for 4 h and at ambient temperature for 39 days. Little change was observed, implying that this photoinduced effect has good thermal stability and a long shelf life under normal conditions.

A dye laser system (Sirah CSTR-6-28 pulsed dye laser, Germany) was pumped at 532 nm by a doubled

Nd:YAG laser (Spectra-Physics Lab-170-10 pulsed laser). A laser dye, DCM, in absolute ethanol, was used for generating a 325-nm UV laser. The period of the phase mask was  $1.0465 \mu\text{m}$ , designed for use at 325 nm. Based on the modulation period and the

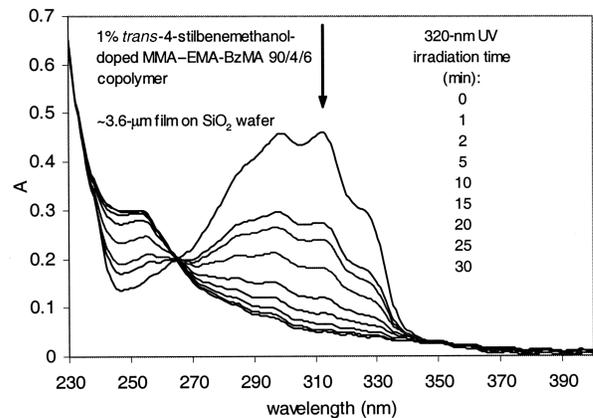


Fig. 2. UV spectra change of *trans*-4-stilbenemethanol-doped core after 320-nm UV irradiation.

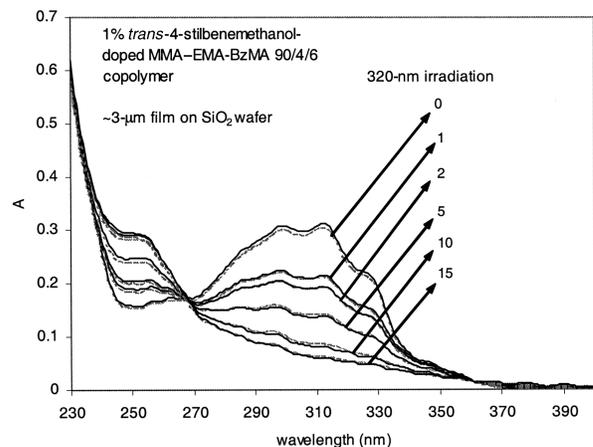


Fig. 3. Effect of covered PMMA layer on UV absorption spectra. Dashed curve, with  $\sim 60\text{-}\mu\text{m}$  PMMA film; solid curve, no cover.

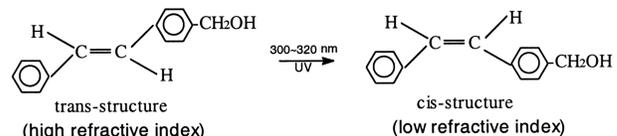


Fig. 4. 4-stilbenemethanol isomerization from *trans* to *cis* structure upon UV irradiation.

**Table 1. Refractive-Index Change for *Trans*-4-stilbenemethanol-Doped Core After UV Irradiation<sup>a</sup>**

Dopant Content (wt. %)	Refractive Index (633 nm)		
	Control Side	Irradiated Side	$\Delta n$
1	1.4991	1.4988	$-3 \times 10^{-4}$
2	1.5021	1.5012	$-9 \times 10^{-4}$

<sup>a</sup>320 nm from UV lamp, 9 min from nine 1-min pulses of exposure.

**Table 2. Description of Grating Formation Process**

POF Specification	Grating Formation Process
Cladding (MMA-BMA 90/10)	325-nm laser, 10 Hz
Core (MMA-EMA-BzMA 90/4/6 + 0.66% wt. <i>trans</i> -4-stilbenemethanol)	10-ns pulse width
Index difference between core and cladding, $\sim 0.011$ (633 nm)	Beam area, $1.2 \times 4$ mm
Fiber optical diameter, $\sim 250$ $\mu\text{m}$	Power, 10 mW
Fiber core diameter, $\sim 20$ $\mu\text{m}$	Scan rate, 0.12 mm/min
	Accumulated exposure time, 10 min
	Grating length, 11 mm

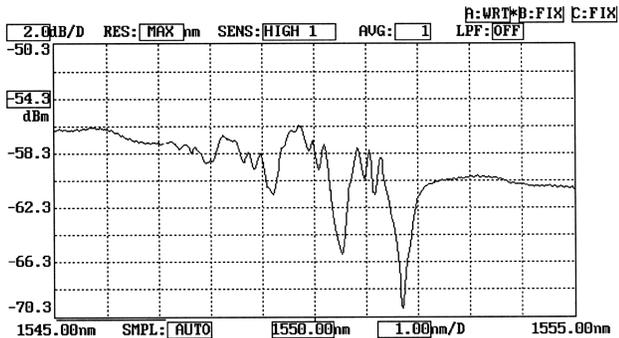


Fig. 5. Transmitted spectrum with grating reflection signals.

refractive index of the core materials, the developed grating has a Bragg wavelength of  $\sim 1550$  nm, a range in which PMMA-based POFs have large transmission loss. Therefore a short-length ( $\sim 70$  mm) fiber sample was coupled to single-mode silica optical fibers with UV curing adhesive (Norland Optical Adhesive 68, Norland Products, Inc.). A broadband LED was coupled to the fiber, and the transmission spectrum was monitored with an optical spectrum analyzer (Ando AQ6330).

Fiber specification and grating formation parameters are described in Table 2. The scanning rate and length were determined by a motion controller. Based on the scanning rate and laser beam width, the accumulated exposure duration was estimated at  $\sim 10$  min. The grating formation was confirmed by the emergence of the reflection peaks in the transmitted spectrum during the grating formation process. The detectable reflection signal was observed after  $\sim 15$  min from the start of the laser scanning (scanning length  $\sim 1.8$  mm). With further scanning the reflection intensity increased steadily. After the completion of the scanning, multiple reflection peaks with different intensities appeared in the spectrum (Fig. 5), which resulted from the few modes present in this fiber. The normalized frequency at 1550 nm, calculated based on the refractive index of the cladding and core and the core diameter, was  $\sim 7.3$ , which is larger than the maximum limit (2.405) for the single-mode condition.<sup>9</sup> Hence multiple modes are expected.

A comparative experiment was conducted on a fiber sample with a similar core component (MMA-EMA-

BzMA copolymer with an 88/4/8 molar ratio) but free of *trans*-4-stilbenemethanol dopant. Although a higher laser power (14 mW) and slow scanning rate (0.03 mm/min, equal to a great accumulated exposure duration of  $\sim 40$  min) were adopted, the reflection signal was not observed when completing the 2.3-mm scanning. But a weak grating reflection signal began to appear several hours later, and its intensity was gradually developed at a slow speed until reaching a saturated state in  $\sim 32$  h. This intensity development process of the reflection signal does not exist in the *trans*-4-stilbenemethanol-doped POF.

A photosensitive PMMA-based POF with a *trans*-4-stilbenemethanol-doped core has been fabricated. Significant change in the UV spectrum of the *trans*-4-stilbenemethanol-doped film was observed as a result of the photoinduced *trans*-*cis* transformation upon 320-nm UV irradiation, and a decrease in the refractive index was detected. A fiber Bragg grating was successfully inscribed in this fiber by use of a 325-nm UV laser with a low photo energy and comparatively short exposure time.

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