Photosensitivity mechanism of undoped poly(methyl methacrylate) under UV radiation at 325 nm and its spatial resolution limit

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Received March 17, 2014; revised April 14, 2014; accepted April 28, 2014;
posted May 1, 2014 (Doc. ID 208422); published June 4, 2014

In this Letter, we provide evidence suggesting that the main photosensitive mechanism of an undoped poly(methyl methacrylate)-based microstructured optical fiber under UV radiation at 325 nm is a competitive process of both photodegradation and polymerization. We found experimentally that increasing strain during photo-inscription leads to an increased photosensitivity, which is evidence of photodegradation. Likewise, refractive index change in the fiber was measured to be positive, which provides evidence for further polymerization of the material. Finally, we relate the data obtained to the spatial recording resolution of the samples.

OCIS codes: (050.2770) Gratings; (060.2310) Fiber optics; (060.3738) Fiber Bragg gratings, photosensitivity; (050.5298) Photonic crystals; (060.4005) Microstructured fibers; (060.5295) Photonic crystal fibers.

http://dx.doi.org/10.1364/OL.39.003421

The photosensitivity of polymers, under UV radiation, is a key factor in the fabrication of optical devices such as gratings or waveguides; for this reason, it is important to understand the different mechanisms involved in optically induced refractive index change (RIC).

One of the most common polymers used for the fabrication of optical devices is poly(methyl methacrylate) (PMMA), because of its good mechanical and optical properties. Both waveguides [1] and gratings [2,3] have been fabricated in it using UV radiation.

The first studies of the photosensitivity of undoped PMMA prepared under special oxidative conditions were made by Tomlinson *et al.* [1] in 1970 and later by Bowden *et al.* [4] in 1974. Both authors achieved similar results, observing an increase of density in the area irradiated by continuous-wave (CW) UV light at 325 nm. However, the two papers proposed different mechanisms responsible for this density increase. Tomlinson proposed an increase of density because of the photo-crosslinking effect, whereas Bowden explained it as a consequence of the photopolymerization of residual monomers using as an initiator peroxides produced during the fabrication process of the PMMA films studied.

Whatever the mechanism, it took a long time (>100 h) to modify the refractive index in the PMMA samples, and consequently, this was not a practical fabrication process for optical devices.

Later, in 1984, Kopietz *et al.* [5] measured the time evolution of RIC in PMMA blocks exposed to a low-pressure mercury UV lamp; they found an initial negative RIC, which subsequently became positive, reaching a saturation value of 0.01. They explained the decrease of refractive index as a consequence of the formation of new monomers, and the later increase as photopolymerization of these monomers. Nevertheless, although they explained the process qualitatively, the chemical reactions involved were not investigated.

The generation of new monomers in PMMA is a consequence of photodegradation of the material. The first studies of the photodegradation of undoped PMMA were done by Torikai co-workers in 1990 [6] and 1993 [7] in air and vacuum, respectively. They demonstrated that PMMA photodegradation occurs at wavelengths below 320 nm; further, they showed that for the longest wavelength studied—320 nm—the primary photochemical reaction was the scission of the main chain of the polymer, forming radicals and monomers. Finally, they obtained similar results in both vacuum and air for an illumination of 320 nm.

No evidence of photodegradation has been reported before in undoped PMMA under UV radiation at 325 nm. However, it is well known that stress produces an increase of the photodegradation effect [8] in polymer samples during irradiation and could allow photodegradation to be relevant at that wavelength.

In this Letter, we provide evidence of the chemical reactions responsible for the main photosensitivity mechanism of undoped PMMA irradiated at 325 nm.

In the experiments we observed that there is an increase of material photosensitivity in samples subjected to higher stress during irradiation, strongly suggestive of a relationship between the photosensitivity mechanism and photodegradation. On the other hand, we found a positive RIC of as much as 8.5×10^{-3}, which implies an increase of molecular weight, providing clear evidence of photopolymerization.

This leads us to hypothesize a competitive process between photodegradation and photopolymerization as being responsible for the photosensitivity. Finally, the photo-inscription resolution limit of the material is discussed.

In order to study the effects mentioned above, a microstructured polymer optical fiber (mPOF) based on undoped PMMA has been manufactured, in which fiber Bragg gratings (FBGs) were inscribed as measurement elements [9].

The fabrication of the mPOF was made in two steps. First, a commercial PMMA rod from GEHR of 60 mm diameter was drilled with a three-ring hexagonal cladding structure with a pitch of $\Lambda = 6.2$ mm and a hole diameter of $d = 2.5$ mm. Then, the rod was fed vertically at a rate of 2.5 mm/min inside a cylindrical oven with a temperature of 290°C and drawn down at a rate of 100 mm/min to a cane with 5.4 mm diameter; this process took around 3 h. The cane was sleeved with three PMMA tubes with outer/inner diameters of 10/7, 15/11, and 20/16 mm to form a new pre-form. This new pre-form was fed into the oven at 290°C at a feed rate of 2 mm/min and then drawn to fiber at a rate of 40 m/min; this process took around three and a half hours. Figure 1 shows an optical microscope image of the cross section of the fiber. The average pitch and hole diameter are 4.26 and 1.87 μm, respectively, and the external diameter is 135 μm. This results in a relative hole diameter of $d/\Lambda = 0.44$; therefore, the fiber could have either a single or a few modes, depending on the wavelength.

A CW He–Cd laser with an output power of 20 mW at 325 nm was used to inscribe the FBGs in the mPOF. The inscription was carried out by using a mirror mounted on a motorized translation stage to scan horizontally with a beam of 1.2 mm diameter focused with a cylindrical lens (focal length approximately 6 cm) along the fiber through a phase mask; these parameters give an average intensity of 900 $\mathrm{kW/m^2}$. The scanning beam velocity was 1 μm/s and the final grating lengths were 1 cm. In order to study the spatial recording resolution of the material, two sets of FBGs were inscribed using two different grating pitches (530.59 and 278.75 nm). Each set was fabricated while the fiber was held horizontally by two clamps under a range of different strains during the inscription; the clamps were separated by 13 cm and the strain was applied by moving one of the clamps using a 3D stage with a displacement resolution of 1 μm. To keep the experiment in the linear viscoelastic regime, a maximum strain of 1% was used [10]. In order to monitor the spectra during grating growth, both ends of the mPOF were connectorized using the method described in [11]. Depending on the grating pitch, one of two broadband light sources was used to illuminate one of the ends (a super-luminescent diode from Superlum centered at 830 nm and an amplified spontaneous emission light source provided by Thorlabs centered at 1560 nm). The other end of the mPOF was connected to an optical spectrum analyzer that had a resolution of 60 pm and a range from 600 to 1700 nm.

Depending on the orientation of the fiber with respect to the UV beam, the optical power reaching the core can vary significantly due to the hexagonal structure in the cladding of the fiber [12]. In order to evaluate and partially compensate for that, three gratings were inscribed for every inscription strain. In Table 1 are shown the gratings' reflectivity (measured in transmission) for the different inscription strains and for both grating pitches. A total of 54 FBGs were fabricated, 27 for each grating pitch.

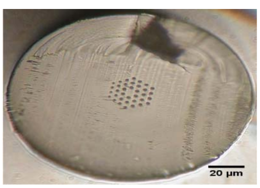

Fig. 1. mPOF cross section.

Table 1. Reflectivity versus Inscription Strain for Grating Pitches of 530.59 and 278.75 nm

	Reflectivity [%]					
	Grating Pitch [nm]					
Strain [%]	278.75			530.59		
0.1	4.5	0.0	1.8	0.0	0.0	0.0
0.2	0.0	3.2	0.5	25.0	20.6	19.3
0.3	22.0	34.2	10.1	23.4	13.3	27.6
0.4	28.0	2.0	3.0	39.0	35.1	21.0
0.5	34.1	58.0	58.3	25.2	41.8	63.3
0.6	66.0	29.0	62.2	70.0	79.0	62.0
0.8	48.7	25.7	29.2	80.3	56.0	99.0
0.9	49.9	69.6	61.5	66.5	88.3	96.9
1	88.6	68.7	88.3	86.3	90.0	85.1

From Table 1, the maximum value of reflectivity for each strain was extracted, corresponding to the maximum transmission of UV light through the microstructured holey cladding into the core. These data are shown in Figs. 2(a) and 2(b) for both grating pitches. It can be observed that there is a strong correlation between the maximum reflectivities and the inscription strain.

From these results, the following was inferred: if grating reflectivity increases with inscription stress, then there is a concomitant rise in photosensitivity as well. According to [8], susceptibility to photodegradation in polymers increases with stress, thereby suggesting that photosensitivity is related to photodegradation. Previous

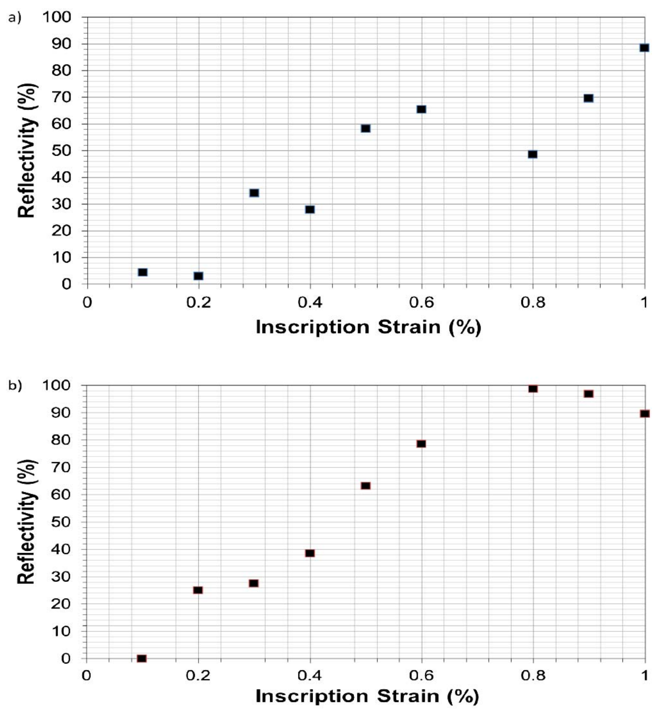

Fig. 2. Bragg reflection against inscription strain: (a) grating pitch of 278.75 nm and (b) grating pitch of 530.59 nm.

studies of photodegradation of PMMA irradiated at 260, 280, 300, 320, 400, and 500 nm found that the longest of these wavelengths causing photodegradation was 320 nm [6,7]. Figure 3 shows the photoreaction responsible for the photodegradation at 320 nm; it corresponds to scission of the main chain and a subsequent creation of monomers, which should lead to a decrease of the average molecular weight. Although the authors say that the photodegradation effect was not observed above 320 nm, the samples were not studied for wavelengths between 320 and 400 nm. In the present work, we used a laser at 325 nm, which we believe is close enough to 320 nm to enable photodegradation to take place.

In order to obtain additional evidence that the irradiated PMMA samples were photodegraded, the RIC produced by UV irradiation of a FBG of 1 cm was measured. The starting point for our analysis is the Bragg condition for FBGs, which relates the resonance wavelength of the grating, λ, to the effective refractive index of the core mode, n_1 [9]:

$$\lambda = 2 \cdot \Lambda \cdot n_1,$$

where Λ is the grating pitch. Once the gratings were inscribed in the mPOF, the phase mask was removed and the UV beam scanned the grating in the same conditions as for inscription (speed beam, spot size, etc.). As a consequence, n_1 is modified in the whole grating and measurement of the resonance wavelength shift allows us to calculate the value and sign of the effective RIC from the Bragg condition; if the resonance wavelength shift is positive, the effective RIC will be positive; otherwise it will be negative. As a first approximation, we can take the effective RIC of the guided mode as the RIC of PMMA. Figure 4 shows the transmission spectrum of two gratings with pitches 278.75 and 530.59 nm inscribed with 1% strain before and after irradiation respectively. For the pitch of 278.75 nm, the index change was 8.0×10^{-3} and for 530.59 nm it was 8.5×10^{-3}.

It is important to note that the irradiated grating did not have the same reflectivity as the original grating; we believe that this is because of the saturation of the index in the material. Moreover, as is clear from Fig. 4, the wavelength shift is positive, indicating a positive RIC and, therefore, an increase of the average molecular weight if density does not remain constant [13]. In [1,4], an increase of the density of PMMA after UV irradiation at 325 nm was measured, implying an increase of the average molecular weight.

According to the hypothesis of Bowden *et al.* [4], photosensitivity of the material arises because of the polymerization of residual monomers using as photo-initiators peroxides formed during the fabrication of the sample. However, Kopietz *et al.* [5] demonstrated an initial

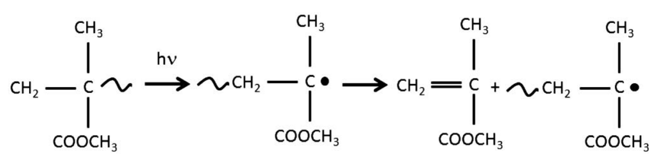

Fig. 3. Photodegradation process of undoped PMMA under UV radiation at 325 nm.

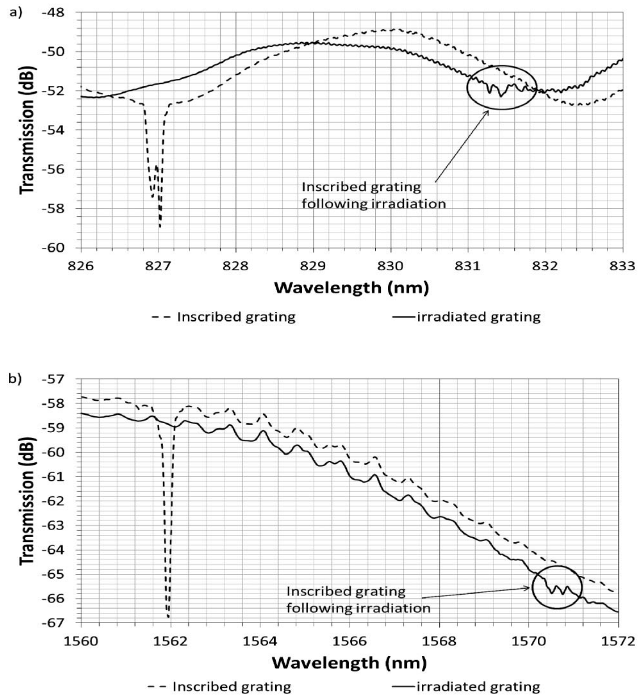

Fig. 4. (a) Index change of an 827 nm grating. (b) Index change of a 1562 nm grating.

formation of a monomer and a later polymerization in PMMA blocks using a broadband UV lamp. In view of our results, we hypothesize that the photoreaction that occurs at 325 nm is a competitive process involving both photodegradation and polymerization effects as in [5]. Depending on the experimental conditions (irradiation time, beam intensity), either polymerization or degradation prevails. In our experiment, polymerization prevails over degradation.

This competitive process follows these two steps: first, the mPOF is irradiated under stress and it is photodegraded, creating new monomers and radicals following the reaction in Fig. 3 (photodegradation is greater at a higher stress as explained in [8]). Second, the radicals formed in the previous step act as initiators of polymerization, interacting with both residual and newly formed monomers to increase the length of the polymer chains.

To study the spatial resolution of the material, the refractive index modulation (RIM) was calculated and compared with the RIC. The RIM can be calculated from the experimental parameters (reflectivity, grating length, etc.) of the inscribed FBGs using the equation [9]

$$R = \tanh^2(K \cdot L) K = \frac{\pi \cdot \Delta n \cdot \eta}{\lambda},$$

where R is the reflectivity of the grating, L is the length of the grating, K is the coupling coefficient, Δn is the RIM, and η represents the fraction of the integrated fundamental mode intensity contained in the core. In the calculation, it has been assumed that $\eta = 1$ and the effective length of the grating is determined by the 1.2 mm beam diameter plus the length scanned by the beam (10 mm), giving a total of 11.2 mm.

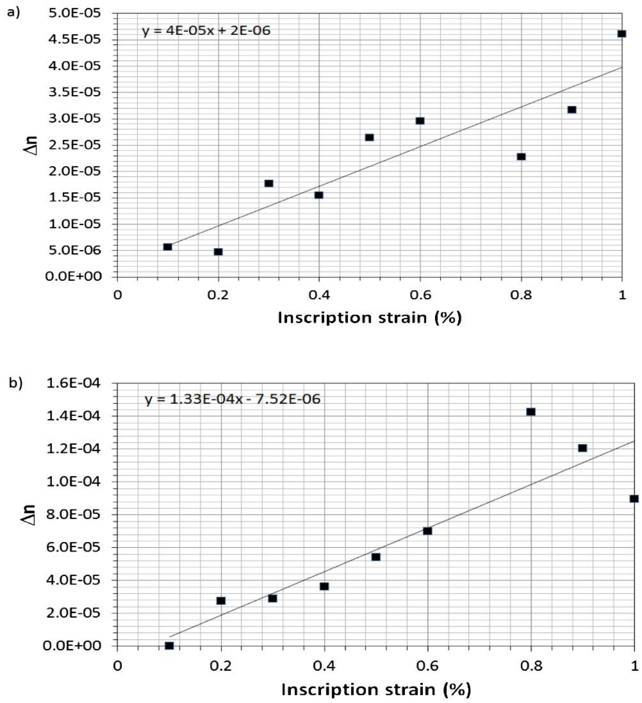

Fig. 5. RIM against inscription strain (a) grating pitch of 278.75 nm and (b) grating pitch of 530.59 nm.

In Figs. 5(a) and 5(b), RIM is plotted against inscription strain for both grating pitches; these data are obtained from gratings with maximum reflectivity for each inscription strain.

As can be observed, the RIM in Fig. 5 for 1% strain does not match with the RIC calculated previously; the difference is almost two orders of magnitude. In view of this result, we can suggest that we are approaching the spatial recording resolution of the material, as explained in [1], due to the polymer chain size.

Gel permeation chromatography was used to measure the number average molecular weight (M_n) of a fiber sample prior to irradiation to allow us to calculate the average chain length. M_n was 140 kg/mol, and considering the molecular weight of one monomer (0.1 kg/mol), we obtain 1400 monomers in the average chain. Taking into account that the molecular length is 0.211 nm [14], the average chain length is around 3 μm. Entanglement of the chains makes the spatial resolution smaller than the chain length, but we would expect to be approaching the spatial resolution limit for the grating pitches used in this work. In particular, we would expect a stronger grating reflectivity for the larger grating pitch and this is confirmed by the data in Fig. 5.

In conclusion, we have studied the photosensitivity of undoped PMMA under UV irradiation at 325 nm for different sample strains. The research helps to unveil the main photoreactions involved in the photosensitivity mechanism. In addition, the RIC has been measured as high as 8.5×10^{-3}, which makes it feasible to fabricate optical devices such as gratings or waveguides. Finally, the spatial resolution limit has been investigated and we have observed a decrease of grating strength as grating pitch becomes smaller because of the polymer chain length.

This work was supported by a Marie Curie Intra European Fellowship included in the 7th Framework Program of the European Union (project PIEF-GA-2011-302919). We also acknowledge the partial support by the EU FP7 under the COST action TD1001. We are very grateful to Paul Topham of Aston University for taking the molecular weight measurement.

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