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Review

# Advances on Polymer Optical Fiber Gratings Using a KrF Pulsed Laser System Operating at 248 nm

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**Abstract:** This paper presents the achievements and progress made on the polymer optical fiber (POF) gratings inscription in different types of Fiber Bragg Gratings (FBGs) and long period gratings (LPGs). Since the first demonstration of POFBGs in 1999, significant progress has been made where the inscription times that were higher than 1 h have been reduced to 15 ns with the application of the krypton fluoride (KrF) pulsed laser operating at 248 nm and thermal treatments such as the pre-annealing of fibers. In addition, the application of dopants such as benzyl dimethyl ketal (BDK) has provided a significant decrease of the fiber inscription time. Furthermore, such improvements lead to the possibility of inscribing POF gratings in 850 nm and 600 nm, instead of only the 1550 nm region. The progress on the inscription of different types of polymer optical fiber Bragg gratings (POFBGs) such as chirped POFBGs and phase-shifted POFBGs are also reported in this review.

**Keywords:** polymer optical fibers; fiber gratings; polymer waveguides

## 1. Introduction

Fiber optic sensors offer key advantages over other sensing technologies, which include immunity to electromagnetic interference, electrical isolation, compactness, being lightweight, and multiplexing capability [1]. Polymer optical fibers (POFs) have been regarded as a viable alternative to silica fibers in a variety of sensing applications. The reason for this is related to the special physical and chemical properties of polymers when compared with silica, leading to additional advantages such as a higher elongation, low Young's modulus, higher thermo-optic coefficient, and the capability to absorb water [2]. Additionally, polymers have biological compatibility and they do not produce sharp edges when broken as occurs with silica fibers, which makes them suitable for in vivo applications [3].

Among the different fiber optic technologies available today, fiber Bragg gratings (FBGs) are pointed out as an interesting device for performing all-optical signal processing and for sensing applications [1]. The combination of FBGs and POFs brings several opportunities, mainly in the sensing domain. The first report of a polymer optical fiber Bragg grating (POFBG) was reported in 1999 by Peng et al. [4], whereas the first long period grating (LPG) reported in POFs was produced by heating a fiber submitted to mechanical stress [5]. Then, a continuous wave laser operating at 325 nm was employed to inscribe LPGs in POF [6]. Since then, the characteristics of POFs, such as the high elastic limit, have been used for the production of high tunable lasers [7] and strain sensors with a high elastic limit [8]. In fact, POFBGs have been applied in several engineering areas, like biomedical [9], civil [10], and biological and chemical [11] spheres. In addition, the fabricated POFBGs can find different sensing applications, such as the capability to measure strain [12], temperature [13], humidity [14], pressure [15], liquid level [16], acceleration [17], and the refractive index [11]. Although there may be some problems in data acquisition such as the wavelength hopping reported in [18] due to sudden changes in the wavelength peak and difficulties with the fiber handling [19], FBG sensors have been employed in applications "outside the laboratory environment". These applications include aviation fuel gauging [20], liquid level sensing in industrial plants [21], and even plantar pressure monitoring systems for biomedical applications [22].

The production of POFBGs has been essentially done through the use of a continuous wave Helium Cadmium (HeCd) laser, operating at 325 nm Ultraviolet (UV) radiation [23]. The technique has been fundamentally employed through the phase mask technique, and several tens of minutes have been reported for the fabrication of a single Bragg grating [3]. Constrains related to the stability of the mechanical apparatus may arise due the size of the structures being created [24]. Additionally, volume fabrication of these structures may be challenging for the future of the technology.

Due the limitations imposed by the time needed to write a single POFBG with the 325 nm UV laser, and knowing that photosensitivity increases for deeper UV wavelengths, it is intended to explore in this review paper, the use of a krypton fluoride (KrF) 248 nm UV laser for the production of POFBGs. The careful control of the laser parameters (repetition rate and energy (E)) will be under analysis, revealing that a POF can be irradiated under an incubation phenomenon, for which there are no signs of polymer ablation [25]. The phase mask method is then employed for the Bragg grating inscription, and the laser parameters are chosen to be within the incubation phenomenon. Results reveal the capability to write a POFBG in tens of seconds, a record time when compared with the conventional HeCd laser. The grating type is analyzed and the refractive index modification will be discussed for uniform, chirped, and phase shifted POFBGs, as well as for the LPGs. The setup is employed for the fabrication of FBGs in other POFs materials, revealing similar results.

Previously, some reviews of POFBG sensors were presented, such as in [1], which presents the operation principle of these sensors, a comparison between POFs and silica fibers, and explains the photosensitivity of POFs. In addition, a review of the FBG inscription in microstructured fibers is presented for both POF and silica fibers in [26], where different holes patterns are presented. A review of POFBG inscription in different POF materials and in different wavelength regions is presented in [27]. Furthermore, it presents the mechanism of photosensitivity in different polymer materials and different POFBGs are also discussed.

Overall, this article intends to first briefly explain the fabrication of POFBGs with the use of the 325 nm and femtosecond (fs) lasers, discussing the advantages and disadvantages. Then, the fabrication of POFBGs using the 248 nm UV laser is presented, where the description of the whole procedure and the explanation of the phenomenon behind the grating growth is under analysis. To provide the full advantages of the inscription system, fibers of different materials and structures will also be described.

## 2. Theoretical Background of FBGs and LPGs

FBGs and LPGs are created through a refractive index modulation when the fiber is exposed to a periodic intensity pattern, where the period of LPGs is much higher than the one of FBGs. In fact, the investigated periods for LPGs are factors of a hundred microns, where the period of FBG is less than one micron. Nevertheless, such modulation can be obtained with the interference of two laser beams [28], where there is a photo-degradation of the polymer when the grating is inscribed [29]. Such photo-degradation is related to the wavelength intensity of the light source employed [30]. Therefore, the rate of photo-degradation is different when the UV source of 248 nm is employed when compared to the one of the 325 nm light source. For some years, the 248 nm laser was not applied to POFBG inscription due to the ablation issues reported in [4]. However, the reason for the ablation reported with the 248 nm laser was the high energy density employed on the grating inscription. Nevertheless, it is possible to obtain a refractive index modification without ablation if a low energy density and repetition rate is employed, which, in the case presented in [31], was 40 mJ/cm$^2$ and 5 Hz, respectively. It was demonstrated a crosslinking between ester side chains of two polymer molecules with a 248 nm irradiation that can result in the increase of the refractive index [31]. This can be related to the lower inscription time of the 248 nm laser when compared to the 325 nm laser. In addition, the polymer starts to photo-degradate as the 248 UV irradiation continues making the material less dense, which leads to a reduction of the refractive index [30]. If the photo-degradation continues, there is polymer ablation, which can be faster if higher energy densities are employed [30]. In order to obtain a POFBG without material ablation and with a lower inscription time, a low energy density with a repetition rate of 1 Hz was employed in [25]. Such pulsed laser parameters enable the inscription of POFBGs at undoped polymethyl methacrylate (PMMA) with only 30 s, which is a lot faster than the lower inscription time for the undoped PMMA fiber obtained with the 325 nm continuous laser (7 min) [24]. For this reason, such a repetition rate was employed in the grating inscription presented in the next subsections. Since the optimal energy density depends on the polymer properties [30], such a parameter was experimentally optimized for the different POF materials.

## 3. State-of-the-Art of HeCd 325 nm Laser Inscription

Although the first POFBG reported was inscribed with both a 325 nm and 248 nm laser, a periodic ablation on the fiber was reported for the 248 nm laser inscription [4]. For this reason, the continuous HeCd laser at 325 nm was the preferred option for gratings inscription applications for many years. The resonance wavelength of such POFBGs is generally around 1550 nm [32] due to the availability of low cost telecom equipment at this wavelength region [33]. Although some polymers are chemically modified by adding different organic combinations, such as the perfluorinated compounds, resulting in the commercially known Cyclic Optical Transparent Polymer (CYTOP) POFs that present low losses on the 1500 nm region [34,35], in general, the materials employed in POFs present higher attenuation losses in this wavelength region [35]. Nevertheless, there is a considerable decrease of the material loss in the wavelength range of 850 nm [36] and with the development of the complementary metal-oxide-semiconductor (CMOS) technology, it is possible to obtain interrogation systems with a lower cost than the one of the 1550 nm region (L band) [3].

For this reason, different POFBGs have been inscribed on the 850 nm (C band) with different POF materials or, in some cases, at the 600 nm region [33]. However, exposure times as long as 100 min with the HeCd 325 nm laser were reported [37], which provide challenges related to the necessity of the higher stability of the setup during an inscription of several minutes [25]. Furthermore, lower inscription times are important for the grating stability [24]. In order to reduce the inscription time for POFBGs, the thermal treatment of annealing was proposed, which comprises keeping the fiber at a temperature close, but below, the material Tg for long periods of time [38]. It is worth mentioning that different annealing treatments were proposed to reduce the annealing time [39] and to reduce the annealing temperature [40], providing a higher range of possibilities for the thermal treatment on the fiber. Another technique for reducing the inscription time is the application of dopants on the POF, which can significantly reduce the inscription time. One dopant commonly applied is the trans-4-stilbenemethanol (TS) that can also increase the grating reflectivity [11,41,42]. Another dopant is the benzyl dimethyl ketal (BDK) that can decrease the inscription time for PMMA POFBGs to about 4 min with an HeCd continuous laser [43].

To date, the PMMA is the most employed material for POFs, which presents a glass transition temperature (Tg) of about 110 °C and high water absorption [23]. In an attempt to obtain a POF with humidity insensitivity, the Thermoplastic Olefin Polymer of Amorphous Structure (TOPAS) fiber was presented in [3]. However, such material presents Tg of only 78 °C that limits its application at high temperatures [23]. In order to overcome this limitation, a different preform of cyclic olefin polymer (TOPAS COC grade 5013) was employed to obtain a Tg as high as 134 °C [23]. In addition, the Zeonex POF was reported in [44] and presents the advantage of better drawability than the other polymer commonly applied in the POF production [44]. Moreover, polycarbonate (PC)-based POFs present higher Tg (145 °C) and can withstand higher strains than the other POF materials presented [8]. The inscription times and central wavelengths for the POF materials mentioned are presented in Table 1, where the continuous HeCd 325 nm laser was employed. To the authors' knowledge, the results presented in Table 1 are the ones with lower inscription times for the HeCd laser. All the POFs were pre-annealed on the results presented.

**Table 1.** Inscription times with different POF materials for the 325 nm continuous laser.

| Material | Inscription Time (min) | Central Wavelength (nm) |
|---|---|---|
| PMMA [24] | 7 | 632 |
| PC [8] | 6 | 879 |
| TOPAS Low-Tg [3] | 58 | 870 |
| TOPAS High-Tg [45] | 4 | 853 |
| Zeonex [44] | 5 | 830 |

Regarding the different types of POFBGs inscribed with the 325 nm laser, a phase-shifted POFBG (PS-POFBG) was proposed in [46], with inscription times lower than 14 min. There is another report of PS-POFBG, where a weak PS-POFBG is presented in the 1550 nm region, but it lacks sharpness in the notch region. In addition, the inscription time for such PS-POFBG is in the order of tens of minutes [47]. To the authors' knowledge, there is no report of chirped POFBG inscribed with the 325 nm laser. In addition, LPG inscription with the continuous 325 nm HeCd laser was firstly reported in [6]. Also, LPGs in POFs were reported in [48], with inscription times of 2 min and 42 s per point for the undoped and TS doped fibers, respectively.

## 4. State-of-the-Art of Femtosecond Laser Inscription

Since they provide higher alternatives for gratings inscription methods, FBGs have been inscribed in POFs using different techniques by means of fs laser. Taking advantage of the shorter pulse times that the fs laser provides, Stefani et al. [49] present a point-by-point technique for POFBG inscription in a microstructured POF (mPOF) made of PMMA. Such a technique allows the direct inscription of the FBG in the fiber core, where an inscription time of 2.5 s was obtained. In addition, the fs laser is employed on the POFBG inscription in CYTOP fibers, which presents lower optical losses in the 1550 nm region than other POFs [10]. For this reason, in 2015, a POFBG was inscribed in CYTOPs fibers both by point-by-point and line-by-line techniques [34].

In order to reduce the multi-peak reflection spectra, the plane-by-plane inscription method was applied to the grating inscription of a graded-index multimode CYTOP fiber in [50], where the same method was also employed in [22]. Recently, the fs laser was applied to the POFBG inscription using the conventional phase mask technique in a TS-doped PMMA step-index POF, where the inscription time of 60 s was obtained [51]. Thereafter, a BDK-doped PMMA fiber was employed and the inscription time was further reduced to 40 s [52]. Despite its higher cost for both acquisition and maintenance, the fs laser presents longer inscription times than the ones obtained in the recent advantages of the grating inscription techniques with the pulsed KrF 248 nm laser, which will be presented in the following sections.

## 5. KrF 248 nm Pulsed Laser Inscription

The necessity of lower inscription times and advances of the polymer photosensitivity characterization and analysis has led to the development of POFBG inscription setups based on the KrF pulsed laser at 248 nm. This section discusses the theoretical background for the POFBG inscription using the KrF 248 nm laser. In addition, it presents POFBGs and LPGs inscribed with the proposed setup.

### 5.1. Fiber Bragg Gratings

Figure 1 presents the experimental setup employed on the POFBG inscription, where a KrF Bragg Star$^{TM}$ Industrial-LN excimer laser operating at 248 nm with a pulse duration of 15 ns is employed, which presents a beam profile of a rectangular Tophat function with dimensions of 6.0 × 1.5 mm$^2$ and divergence of 2 × 1 mrad$^2$. The setup also presents mirrors, focal lens, and a slit with a 4.5 mm width for positioning the UV beam on the phase mask employed, which is focused onto the fiber core through a plano-convex cylindrical lens (Newport CSX200AR.10, Newport, Irvine, CA, USA) with an effective focal length of 200 mm. The setup presented results in an effective spot size on the fiber with a width of 20 mm and a height of 32.4 µm. In addition, 3D translational stages are applied in order to obtain the correct positioning of the fiber. Also, the translational stages avoid fiber bending during the inscription.

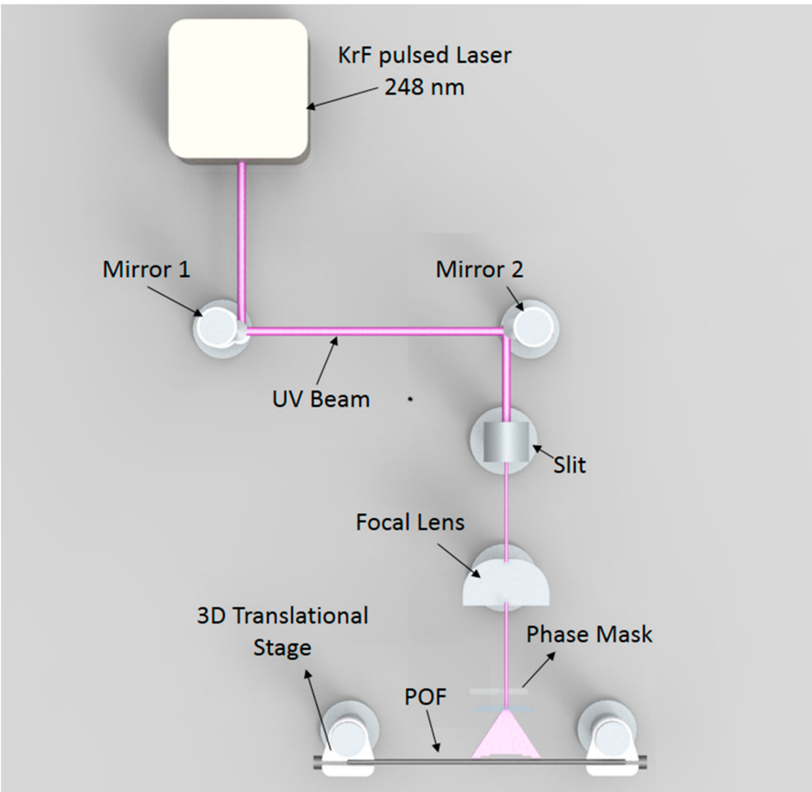


**Figure 1.** Inscription setup with the KrF pulsed laser at 248 nm for the POFBGs.

The presented setup is employed for the inscription of uniform POFBGs, chirped POFBGS, and PS-POFBGs. The differences of these POFBGs are related to refractive index variation along the fiber length ($z$-axis), where in the uniform POFBG, the period ($\Lambda$) is constant. Whereas, for the chirped POFBG, there is linear aperiodic grating with the period variation along the $z$-axis. Regarding the PS-POFBG, there is a phase shift that modifies the period in a certain length of the fiber along the $z$-axis. In order to illustrate such variations of the refractive index, Figure 2 presents the period of each type of POFBG with respect to the fiber $x$-axis, where Figure 2a represents the uniform POFBG, and Figure 2b,c present period variation of the chirped and PS-POFBGs, respectively.

Regarding the uniform POFBGs, Oliveira et al. [25] employed a similar setup with the 248 nm KrF pulsed laser to inscribe POFBGs at the 1550 nm region for a PMMA POF. In addition, the setup presented in Figure 1 was employed to inscribe POFBGs in different POF materials at the wavelength region of 850 nm. It obtained an inscription time lower than the one presented in [25] for the PMMA POF and lower inscription times than the ones obtained with the 325 nm continuous laser for TOPAS high and low-Tg, PC, and Zeonex fibers. Table 2 presents the inscription times for different POF materials employing the experimental setup presented in Figure 1 at the 850 nm region. It is worth mentioning that all the POF samples were pre-annealed for 24 h on temperatures close, but below, their Tg, since such heat treatment can reduce the inscription time [38].

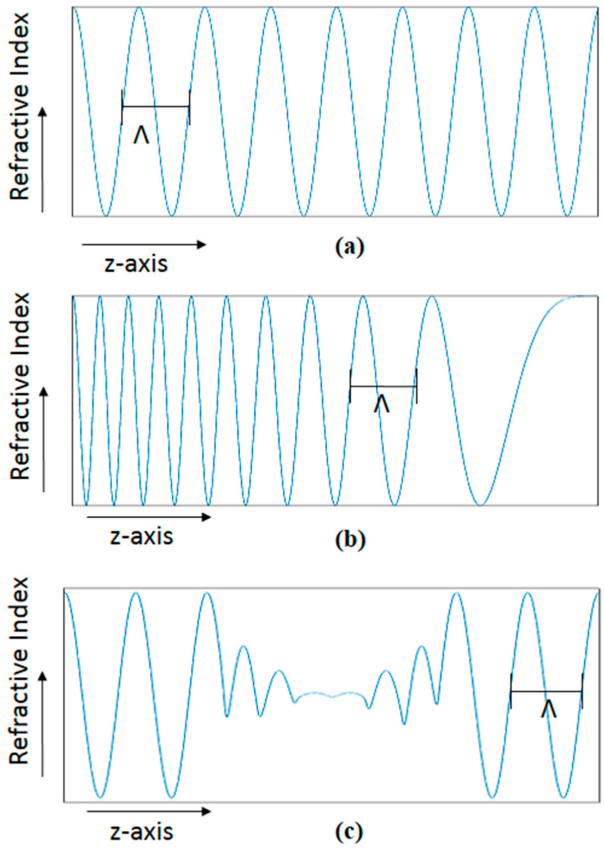


**Figure 2.** Periodic variation of the refractive index with respect to the fiber *z*-axis (fiber length). (**a**) Uniform POFBG; (**b**) Chirped POFBG; and (**c**) PS-POFBG.

**Table 2.** Inscription times in the 850 nm region with different POF materials for the 248 nm pulsed laser.

| Material | Inscription Time (s) |
|---|---|
| PMMA | 25 |
| PC | 14 |
| TOPAS Low-Tg | 25 |
| TOPAS High-Tg | 20 |
| Zeonex | 15 |

Furthermore, it was possible to inscribe uniform POFBGs with the 248 nm pulsed laser at the wavelength region of 600 nm for the first time. Figure 3a presents the reflection spectrum of the uniform POFBG inscribed with one pulse on a BDK-doped PMMA POF that presents a central wavelength of about 603 nm, a reflectivity of 15 dB, and a bandwidth of 0.1 nm. Whereas, Figure 3b shows another POFBG inscribed with a different phase mask with a central wavelength of 668 nm, a reflectivity of 14.3 dB, and a bandwidth of 0.1 nm, and the same POFBG was subjected to a post-annealing treatment at 70 °C (with 90% relative humidity) during 10 h. The annealing leads to a blue-shift of more than 30 nm and a slight increase of the grating strength.

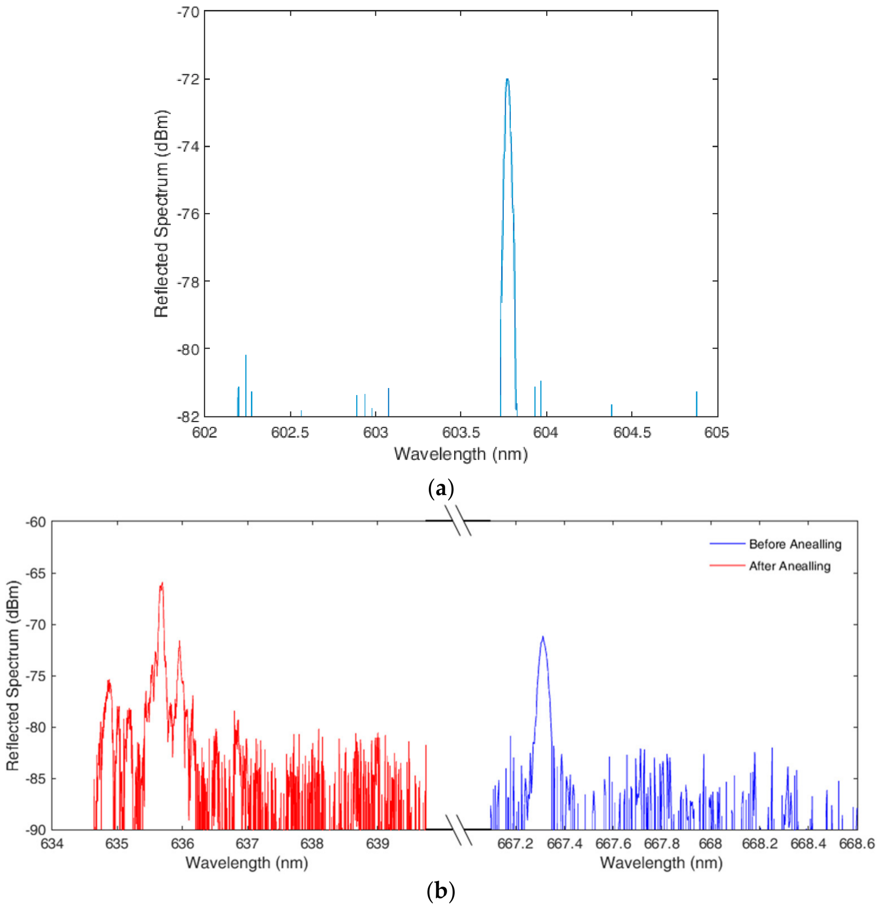


**Figure 3.** (**a**) Reflection spectrum of the uniform POFBG inscribed at 604 nm with the KrF pulsed laser 248 nm; (**b**) Reflection spectrum of the uniform POFBG inscribed at 667 nm and the same grating after the post-annealing process.

Another breakthrough concerning the reduction of inscription times is related to the possibility of doping the fiber. Such dopants can increase the POF photosensitivity, which leads to a significant reduction of the inscription time. Among the BDK and TS dopants cited in Section 2, the BDK is a photo-initiator, which presents an absorption coefficient higher at wavelengths shorter than 325 nm that leads to a very fast triggering of the photo-polymerization on the fiber. By adding BDK on a PMMA POF, it was possible to produce a uniform POFBG with a single laser pulse with the KrF 248 nm laser [30], which represents an inscription time in the order of 15 ns. In order to clarify and present some breakthroughs related to the enhancement of the inscription time of uniform POFBGs, Figure 4 presents the historical evolution of the POFBGs inscription time with the phase mask technique, where some reasons or breakthroughs related to such evolution are presented. The goal here is to present the evolution inscription time reduction throughout the years. Since the POFBGs inscription with the fs laser by the phase mask technique was only recently reported and presented inscription times longer than the ones of the KrF laser, such results with the fs laser are not presented, but it is worth mentioning that inscription times as short as 40 s are reported [52].

Different types of POFBGs have been inscribed with the setup presented in Figure 1. The first chirped POFBG on undoped fiber was inscribed with a chirped phase mask, where its responses with respect to the temperature, strain, and pressure were characterized [53]. However, by applying a chirped phase mask, the chirp parameters of the grating are limited to the ones of the phase mask and different chirped phased masks are necessary to obtain different chirp parameters, which can make the technology very expensive. For this reason, a different technique to obtain chirped POFBG was proposed in [54]. The technique relies on tapering the POF to obtain the chirp, which is obtained by the fiber etching on a container filled with acetone. Such a process greatly improves the flexibility on chirped POFBGs manufacturing. In addition, a BDK-doped POF was employed in [54] and the chirped POFBG was obtained with a single laser pulse using a uniform phase mask. Figure 5 presents the reflection spectrum of the chirped POFBG inscribed with the method described. In order to show the chirped POFBG tuning with strain, Figure 5 presents the same chirped POFBG when a strain of 0.3% and 1.85% is applied. Note that the grating was inscribed with a 0.3% strain, so when we released or applied strain, we could achieve different chirp values.

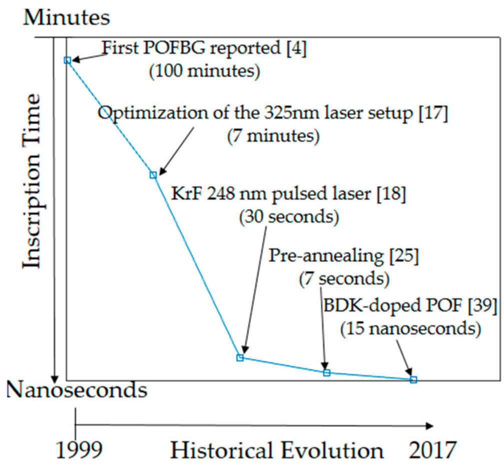


**Figure 4.** Historical evolution of the uniform POFBG inscription time with the phase mask technique for HeCd and KrF lasers.

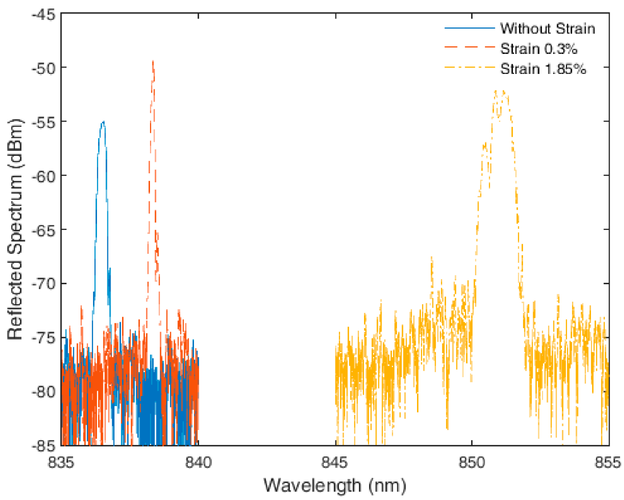


**Figure 5.** Chirped POFBG inscribed with a uniform phase mask by tapering the POF under different strain conditions as presented in [54].

The KrF 248 nm pulsed laser was also employed in the inscription of PS-POFBGs, where a metal wire divides the laser beam, which leads to the creation of a phase shift on the Bragg grating [15] (see Figure 6). The possibility of creating multiple phase shifts on the grating with additional metal wires in the laser beam was also demonstrated. However, it may be difficult to position the metal wires correctly due to the low dimensions of the laser beam and phase mask. In order to overcome this limitation, a PS-POFBG fabricated by overlapping two uniform FBGs with different periods to create a Moirè grating was proposed in [55], where the addition of more FBGs can lead to the creation of additional phase shifts in the POFBG. In addition, the PS-POFBG proposed in [55] was inscribed with only two pulses of 15 ns each.

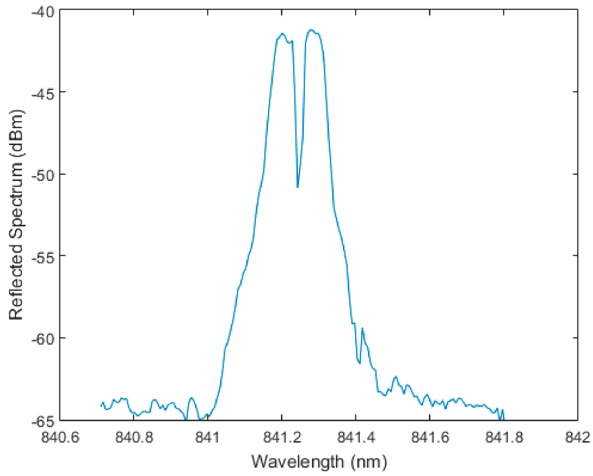


**Figure 6.** PS-POFBG inscribed by positioning a metal wire in the laser beam presented in [55].

### *5.2. Long Period Gratings*

The refractive index periodic variation with respect to the fiber length ($z$-axis) of an LPG is similar to the one presented in Figure 2a, where the period of the LPGs is some orders of magnitude higher when compared with uniform POFBGs.

A fast LPG inscription on POF is reported in [56], where the KrF pulsed laser was employed in a setup similar to the one presented in Figure 1 in a BDK-doped PMMA POF using a point-by-point technique. Two UV-pulses of the laser were employed to inscribe the LPG at each point, which led to a reduction in the inscription time of about 21 times when compared with the inscription time reported for a TS-doped PMMA POF with the HeCd 325 nm continuous laser [48]. The LPG presented a length of 25 mm with a peak strength of -20 dB, as presented in Figure 7.

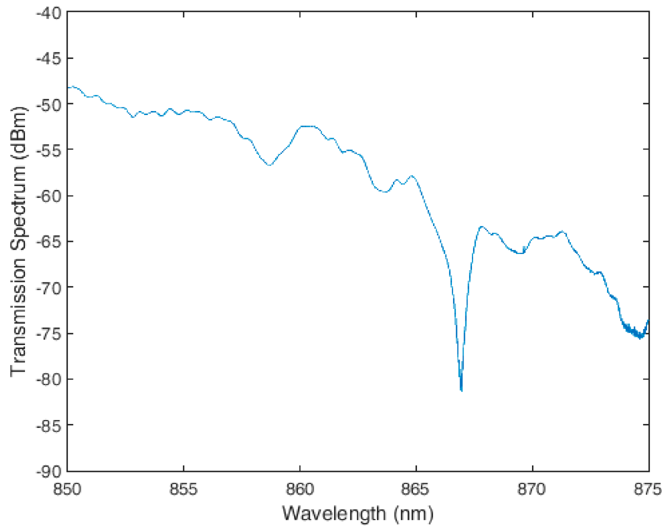


**Figure 7.** Transmission spectrum of the LPG inscribed with the KrF pulsed laser 248 nm as reported in [56].

## 6. Final Remarks

The POF grating inscription is a growing research field where significant progress has been made. Inscription times higher than one hour that were reported in the early 2000's are now in the order of seconds for undoped POFs and nanoseconds for doped fibers. In addition, different POF materials such as PC, Zeonex, and TOPAS have been investigated to overcome some issues of PMMA material, such as water absorption and low Tg. One of the key aspects of this evolution of POFBG and LPG inscription is related to the investigation of the polymer photosensitivity in shorter wavelengths and on the study of the polymer ablation that enables the application of 248 nm pulsed lasers. Furthermore, progress has also been made regarding the wavelength regions where the fiber gratings can be inscribed, which are not only the commonly applied 1550 nm region, but also the 850 nm and 600 nm regions. Such significant progress on the grating inscription, material characterization, and fabrication can enable the application of POFBGs in commercial applications as a complement to the commonly employed FBGs in silica fibers. It is possible that in a few years, some commercial applications of POF gratings will be reported.

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**Author Contributions:** C.M., A.L.,-Jr, R.M. and M.D. performed the experiments and were involved in the results analysis and paper-writing. C.L., P.A. B.O., and P.A. were focused on the results analysis, literature review, and paper-writing.

**Conflicts of Interest:** The authors declare no conflict of interest. The founding sponsors had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript, and in the decision to publish the results.

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