

## **BIREFRINGENCE GRATING WITHIN A SINGLE MODE POLYMER OPTICAL FIBRE WITH PHOTSENSITIVE CORE OF AZOBENZENE COPOLYMER**

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A single mode optical fibre with a core of azobenzene-containing copolymer instead of doped polymer was fabricated. A 120  $\mu\text{m}$  long-period birefringence grating with a 50% duty cycle has been successfully written within the core of the fibre with 532 nm laser by a mask method. Under polarized microphotography, the grating was observed when the optical axis was set at 45° with the direction of the first polarizing lens of the polarization microscope. Although birefringence decayed gradually when writing laser was turned off, a permanent change of refractive index as much as  $7.0 \times 10^{-4}$  still has been observed in the material, which ensures the stability of written birefringence grating.

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### **1. Introduction**

Since the first report of Hill et al. in 1978 [1], the fiber grating became a very attractive optical device in high-performance optical communication systems. In addition to the application where the gratings are used as reflectors, e.g. wavelength tuning and optical fiber sensing, there are two other major applications of fibre gratings. In these applications, the grating period is modulated by external environment such as strain and temperature. For silica optical fibre gratings, some of which have been commercialized, the change caused by the external actions is small due to the small coefficient of thermal expansion and the large Young's modulus of silica glasses. For example, a report on a magnetically tunable fibre Bragg grating for a reconfigurable optical add-drop multiplexers demonstrated a 4 nm shift of the Bragg wavelength [2]. Different from the silica glass, polymer is characterized by its soft material properties. For example, the Young's modulus of silica ( $7.1 \times 10^{10} \text{ N/m}^2$ ) is 70 times that of poly(methyl methacrylate) (PMMA) ( $1 \times 10^9 \text{ N/m}^2$ ) [3], and the thermal expansion coefficient of silica fibre ( $5.5 \times 10^{-7} \text{ K}^{-1}$ ) is about one hundredth of that of PMMA fiber ( $8.0 \times 10^{-5} \text{ K}^{-1}$ ) [4]. By stretching, a polymer optical fibre (POF) grating has shown a shift of 74 nm in its Bragg wavelength, far larger than 4 nm of the silica glass fiber given above [5]. Moreover, because of the excellent compatibility of base POF materials with many functional organics, special POFs are developed in recent decades for various active photonic devices, such as all-optical switches [6-8], amplifiers [9-11], as well as POF gratings [12,13].

Commonly, there are four mechanisms that can lead to the creation of gratings in POF by

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means of light: ablation, chain scission, cross-linking, and photopolymerization [14], and many works concerning POF gratings are based on the last two mechanisms reported before. Recently, based on the azobenzene dye doped polymer, a birefringence grating in a multimode POF was developed in our group by the mechanism of photoinduced alignment of azobenzene units [13]. In this paper, in order to overcome the immigration of azobenzene dye and make the POF grating compatible with other photonic devices, a single mode POF, using azobenzene copolymer as POF core instead of azobenzene doped polymer, was further developed and a birefringence grating was demonstrated in the POF based on the polarized light induced birefringence by the mask technique. In this paper, in order to overcome the immigration of azobenzene dye and make the POF grating compatible with other photonic devices, a single mode POF using azobenzene copolymer as POF core instead of azobenzene doped polymer was further developed, and a birefringence grating was demonstrated by the mask technique in the POF based on the polarized light induced birefringence with a relatively cheap 532 nm Nd:YVO<sub>4</sub> laser, which provided more potential for commercial production.

## 2. Experimental

### 2.1 Synthesis of azobenzene monomer

**4-cyano-4'-hydroxy azobenzene** A solution of sodium nitrite (13.8g, 0.2 mol) in 50ml of water was added dropwise at 0 °C to a mixture of 4-cyano-aniline (23.6 g, 0.2 mol) and 50 ml 36.5% hydrochloric acid (0.6 mol) in 300 ml water. After the obtained suspension solution was stirred at 0 °C for 1hr to produce the diazonium salt, the mixture was filtered with a Butcher funnel. A solution of phenol (18.8 g 0.2 mol) and sodium (8.0 g, 0.2 mol) in 100 ml water was added dropwise at 0 °C to the above filtrate. After the mixture was stirred at 0 °C for 5 min the mixture was neutralized with sodium acetate and stirred for another 10 hr at 0 °C, and then the produced precipitate was collected and washed with excess water. After removal of the water, the product was purified by recrystallization from a mixture solvent of DMF and water (1: 1)

**4-cyano-4'-(2-hydroxy-ethyl)-azobenzene** A mixture of 4-cyano-4'-hydroxy azobenzene (22.3g 0.1 mol) and 2-chloroethanol (10 ml, excess) was dissolved in DMF. Potassium carbonate (14 g 0.1 mol) and a spatula of potassium iodide (as catalyst) were added into the solution. The resulting mixture was heated at 120 °C and kept stirring for 48 hr. Reaction was stopped by addition excess water in to the mixture. Large amount of crude product was precipitated. The produced precipitate was collected and washed with excess water. After removal of the water, the product was recrystallized with ethanol.

#### **2-{4-[2-(4-cyano-phenyl)-diazenyl]-phenoxy}-ethyl methacrylate(CAMA)**

4-cyano-4'-(2-hydroxy-ethyl)-azobenzene (14g 0.05 mol) was dissolved in 250 ml dried dichloromethane, DCC(26 g, 0.1 mol ) and DMAP (2g) (as catalyst) and methacrylic acid (4.3 g, 0.05 mol ) was added to the solution. After the mixture was stirred at room temperature for 24 hr, the mixture was filtrate by using a Butcher funnel and the precipitate was washed with dichloromethane three times. Filtration was collected. The crude product was obtained by removal the dichloromethane by using a rotatory evaporator. The crude product was purified again by column chromatography on silica gel with a mixture solvent of chloroform and methanol (9:1) as eluent to give the title compound CAMA. <sup>1</sup>HNMR(CDCl<sub>3</sub>):δ 7.7-8.0(m 6H, CH in aromatic ), 7.0-7.1(d 2H, CH in aromatic), 6.18 (s H, C=CH), 5.62 (s H, C=CH), 4.54-4.57(t 2H, OCH<sub>2</sub>),4.3-4.35(t 2H, OCH<sub>2</sub>), 2.0 (s 3H, C=CCH<sub>3</sub>). FTIR: cm<sup>-1</sup>: 2923 (δ<sub>CH</sub>), 2227, (δ<sub>CN</sub>), 1729(δ<sub>C=O</sub>), 1599(δ<sub>C=C</sub> in aromatic ring) 1499 (δ<sub>C=C</sub> in aromatic ring), 1253(δ<sub>N=N</sub>), 1139 (δ<sub>C-O</sub>).

### 2.2 Fabrication of single mode POF

To fabricate a photosensitive single mode POF, a hollow stick was made from copolymer of methyl methacrylate (MMA) and butyl acrylate (BA) according to the procedure reported before [15]. Then, 10 ml MMA, 0.4g CAMA, 30 mg benzyl peroxide as an initiator, and 15 μ L n-butyl

mercaptan as a chain-transfer agent were mixed in a vessel. The above solution was prepolymerized in a sealed tube under vacuum, then the prepolymer transferred to a balance dropping funnel, as shown in Fig. 3. The set up was connected to a vacuum system to remove the air. Then the prepolymer was filled into the hollow stick drop-wisely under vacuum condition as a core material, The thermal polymerization of the filled stick was carried out in an oven under 5 atm  $N_2$ . The temperature of the oven was increased gradually from 40 °C to 120 °C in seven days until solidification was fulfilled. The preform prepared by this process was then heat-drawn into an optical fiber at 110 °C by a taking up spool.

### 2.3 Writing of the fibre grating

To write a birefringence grating within a POF, 20 mW, 532 nm laser was directly irradiated to the fibre through a deflective mirror and an amplitude mask at temperature 20 °C. The polarization direction of the irradiation is set parallel to the optical axis of the mask. The pump beam spot was 0.2 cm<sup>2</sup>. A deflective mirror was fixed on a scanning setup. In experimental the mirror was moved along the direction parallel to the fibre to obtain a grating with desired length.

### 2.4 Study of the photoinduced birefringence and estimate of $\Delta n$

The film sample was used to study the photoinduced birefringence and estimate  $\Delta n$ . To prepare the copolymer different amount of CAMA was firstly mixed with MMA, and then polymerization was conducted in DMF with BPO (3% by mol) as initiator and n-butyl mercaptan(0.15% by wt) as a chain-transfer agent. The solution of polymerization was first precipitated in excessive methanol after the polymerization ended. The polymer obtained was dissolved in THF, and then purified by precipitation in a large excess of methanol. The process was repeated for three times. To prepare the copolymer film sample, a copolymer of the core material was dissolved in cyclopentanone, then the solution was casted on a fresh silica surface. To prepare the doped sample, different amount of 4-cyano-4'-(2-hydroxy-ethyl)-azobenzene and pure PMMA was dissolved in cyclopentanone, then the solution was casted on fresh silica surface.

The experimental setup for the study of the photoinduced birefringence and estimate the  $\Delta n$  are similar to that described in reference [16]. The frequency doubling Nd:YVO<sub>4</sub> laser ( $\lambda = 532$  nm) was used as a pump beam and the probe beam was provided by a diode laser (650 nm). The linearly polarized probe beam passed through the film sample and a crossed polarizer. The angle between the polarization direction of the pump beam and that of the probe beam was set to 45°. The transmission power of the probe beam was measured with a Newport-channel Power Meter (Model-2832c), and the data were recorded with a computer. The operation temperature was about 20 °C.

## 3. Results and discussion

From the point of view of physical structure, POF is composed of two layer materials: the out-layer called cladding and the inner-layer called core. To obtain a stable and applicable POF grating, some criteria in material and structure of POF should be taken into consideration during designing, which include: (1) Core material of POF must be of higher refractive index than cladding material and photosensitive only at a given wavelength, which is not photosensitive to the cladding material and not within the optical window of POF; (2) The photosensitive units must be connected with polymer by chemical linking in order to get a stable refractive index modulation in dimension and time scale; (3) Absorption of core material for the irradiation light used to write gratings must be low enough to get bulk gratings; (4) For application, a single mode POF is needed, other than a multimode POF, to get a high reflectivity of POF gratings. Azobenzene units are attracting candidates according to the above criteria. The most important merit of the azobenzene molecules is the reversible trans-cis-trans photoisomerization with respect to the  $N=N$  double bond, which can induce the anisotropy in azobenzene polymers. This feature has been widely used to fabricate surface gratings and birefringence gratings. However, in order to get bulk gratings in POF,

absorption of irradiation light by core material should be as low as possible. Based on the previous work [13], irradiation light with wavelength at 532 nm was adopted in this work, although 7-10  $\mu\text{m}$  thick cells were typically adopted to fill azobenzene liquid crystalline polymers to perform photoinduced orientation with light at other wavelength [17].

Homopolymer containing azobenzene moieties is not suitable to be used as POF core materials because micro-domain formed within the liquid crystalline polymer can result in scattering of light passing through POF. On the other hand, it has been found that grating obtained from a POF with a core of azobenzene doped polymer is not stable [13]. The polymer used in this work was designed to have short spacer and copolymerized with methyl methacrylate (MMA) to overcome the above deficiencies. Fig. 1 shows the structure and the absorption spectrum of the copolymer adopted in this work, showing the two absorption peaks located at 266 nm and 366 nm ascribed to the absorption of aromatic ring and  $n \rightarrow \pi^*$  of  $\text{N}=\text{N}$  bond, respectively.

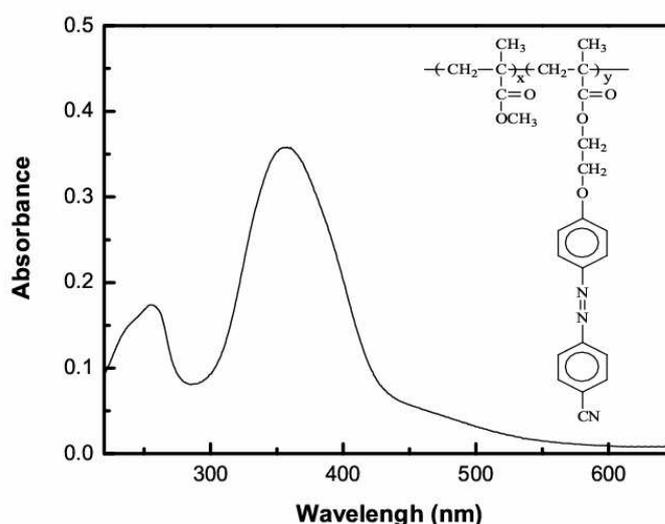


Fig. 1. Absorbance spectrum and chemical structure of azobenzene containing copolymer used as POF core material.

Under condition of low azobenzene concentration, the copolymer is amorphous, as shown by X-ray diffraction (see inset in Fig. 2). When the sample film was irradiated with a 532 nm wavelength polarized light, photo-induced birefringence and relaxation were observed as shown in Fig. 2, for doped polymer and copolymer respectively. It is obvious that an almost equally fast growth of birefringence occurred for both copolymer and doped polymer at the beginning of irradiation, reaching an approximate saturation value at about 30 minutes. However, after switching off irradiation light the birefringence was estimated at 60% at this concentration (the permanent birefringence corresponds to  $t \rightarrow \infty$ ) much higher than that of the doped sample at the same azobenzene concentration. Differences between doped samples and copolymer samples with different azobenzene content have also been studied, and the results are listed in Table 1, in which the results show that the birefringence increases with the increasing of azobenzene concentration for both kind of samples and permanent  $\Delta n$  is higher for the copolymer than that of doped samples at the same concentration. It is worth to note that for doped samples the concentration of azobenzene can not be over 1 % by weight, because further increasing concentration of the dopant will result in a serious scattering due to the microcrystals of azobenzene compound. No such a phenomenon is produced in copolymer samples.

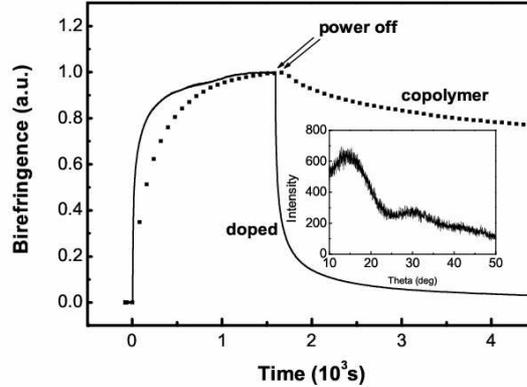


Fig. 2 Relationship between the birefringence and time for doped material and copolymer. The concentration of azobenzene moiety is 1% by weight. The pump power is 23 mW, and the pump beam spot is  $0.5 \text{ cm}^2$ . Inset: XRD of azobenzene containing copolymer, concentration of azobenzene moiety is 4% by weight.

POF usually can be made with a large diameter and multimode due to soft nature of polymer, which satisfies many special demands in application. However, in order to have a high reflectivity and to be compatible with other photonic devices, a single mode POF is preferability condition for fabricating POF gratings. The mode number is related to several parameters of the material from which POF is made, and the relationship among the parameters should obey the following equation [18]:

$$\frac{2\pi}{\lambda} \cdot a \sqrt{n_{co}^2 - n_{cl}^2} < 2.4 \quad (1)$$

in which,  $n_{co}$ ,  $n_{cl}$ ,  $a$ , and  $\lambda$  are refractive index of core, refractive index of cladding, radius of core and working wavelength, respectively. Obviously, in order to get a single mode POF, the azobenzene concentration related to  $n_{co}$  and  $\Delta n$  should be controlled in terms of the diameter of the POF core. Table 1 has given the relationship among concentration of azobenzene,  $\Delta n_{max}$ ,  $\Delta n_{perm}$  and theoretical estimation of corresponding diameters. Taking all the effects into consideration, 4% by weight of azobenzene concentration was estimated.

Table 1 Relationship between material nature and parameters of single mode POF\*.

Sample No	Concentration of azobenzene (% by wt)	$\Delta n_{max}$ ( $10^{-4}$ )	$\Delta n_{perm}$ ( $10^{-4}$ )	Radius for single mode for 1550nm ( $\mu\text{m}$ )	Material nature
1	0.08	0.3	0.03	28	Doped
2	1	4	0.16	8.0	Doped
3	1	3.1	1.9	8.0	Copolymer
4	4	10.0	5.2	3.9	Copolymer
5	10	24	11	2.5	Copolymer.

\* the method to calculate the  $\Delta n_{max}$  and  $\Delta n_{perm}$  will discussed at later part of this paper.

Single mode POF was made by a method schematically shown in Fig. 3. Due to the small diameter in core, single mode POF with typical applications is usually made by special techniques,

such as single mode nonlinear POF [19], single mode electrooptic POF [20] and single mode microstructure POF [21]. In this work, the POF fabrication employs a two-step process, which is similar to conventional POF fabrication techniques except that, in order to avoid excess air especially excess oxygen dissolved into prepolymer, the prepolymer was freely dropped into the hole of a PMMA stick under vacuum environment as shown in Fig. 3. The hollow stick was made according to the method reported before [15], and the bottom opening was closed over when operating. To get a single mode POF, the inner diameter of the stick was controlled to be  $100\ \mu\text{m}$ . By this technique, a preform with an 18/1 ratio of preform diameter to core diameter was obtained, which had a homogeneous copolymer core after fully polymerization. The ratio was kept constant during fibre drawing process, and a single mode POF with azobenzene core was obtained with a core diameter of  $6\ \mu\text{m}$  and a fiber diameter of  $114\ \mu\text{m}$ .

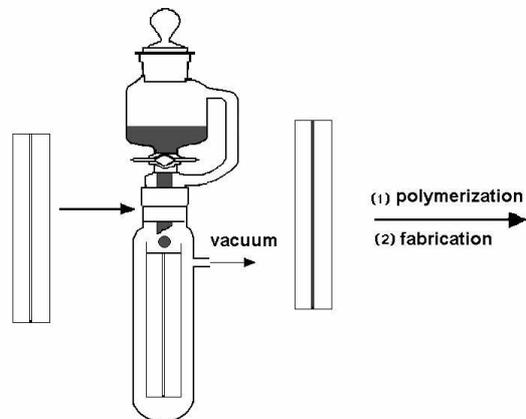


Fig. 3. Schematic sketch for fabricating single mode POF.

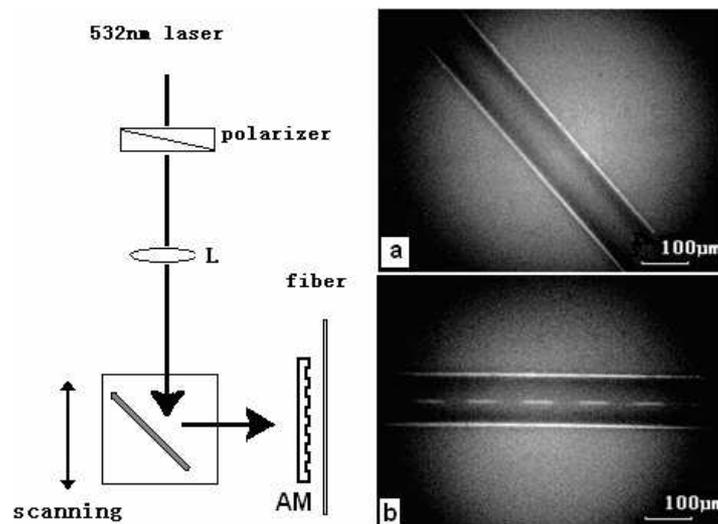


Fig. 4. Experiment setup for writing birefringence gratings and polarized photograph of the grating in a single mode POF. (L = cylindrical lens, AM = amplitude mask) a:  $\theta = 45^\circ$ , b:  $\theta = 0^\circ$ , and  $\theta$  is the angle between fiber and the polarizer of polarization microscope.

Before writing grating, the entire POF is homogeneous and no any orientation of azobenzene moieties within the core material as indicated by polarization microscopy photo similar to Fig. 4-a. The experiment setup for writing grating by a amplitude mask method is also schematically shown in Fig. 4. The period and duty cycle of the mask were  $120\ \mu\text{m}$  and 50%, respectively, and the optical axis of the birefringence grating was perpendicular to the polarization direction of pump beam. When the fibre was rotated to make the optical axis be  $45^\circ$  with the

direction of the polarizer of polarized microscope, the birefringence grating can be seen clearly (Fig. 4-b). When the optic axis of the grating was parallel or perpendicular to the direction of the polarizer of polarized microscope, the grating patch in the fibre can not be detected as shown in Fig. 4-a. This indicates that the fibre grating is a birefringence grating, and is much more stable as compared with previous work using azobenzene doped polymer as core materials.

In order to estimate the  $\Delta n$ , film samples with the same material as core were prepared, and an experimental set up reported before [5] was used to study the photo-induced birefringence and to estimate the  $\Delta n$ . Once the linearly polarized pump beam irradiating, the birefringence is induced in the polymer films. Part of probe light will pass through the two crossed polarizers. According to Jones matrix method [22], the  $\Delta n$  is given by the following equation:

$$\Delta n = \lambda \cdot \arcsin(\sqrt{I/I_0})/\pi h \quad (2)$$

Here,  $\lambda$ ,  $I_0$ ,  $I$ , and  $h$  are wavelength of probe light, intensity of incident light, intensity of transmitted light and thickness of the film, respectively. For the experimental data:  $I_0 = 4.25$  mW,  $I = 1.5$  mW,  $h = 60$   $\mu\text{m}$ ,  $\lambda = 0.65$  substituted and fitted to Eq. 2, the maximum change of the refractive index  $\Delta n = 1.04 \times 10^{-3}$  can be obtained.

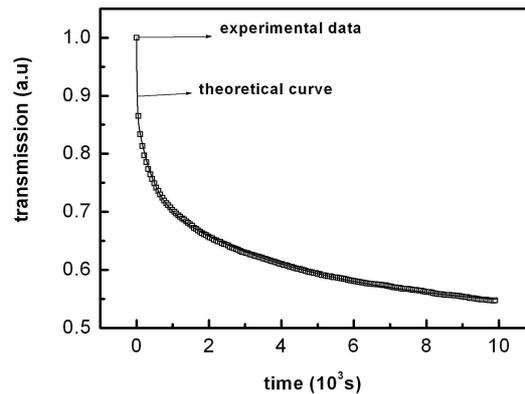


Fig. 5. Dependence of the birefringence upon the time after the pump beam was turned off.

When the pump beam was turned off, the birefringence decreased gradually. Fig. 5 shows the dependence of the birefringence upon the time after the pump beam was turned off. To estimate the permanent  $\Delta n$ , the experimental data was accurately fit to a following normalized tri-exponent equation:

$$y = C \exp\left(\frac{-t}{t_1}\right) + D \exp\left(\frac{-t}{t_2}\right) + (1 - C - D - E) \left(\frac{-t}{t_3}\right) + E \quad (3)$$

Here,  $t_1$ ,  $t_2$ ,  $t_3$ , are time parameters corresponding to different disorientation processes.  $C$ ,  $D$  and  $1-C-D-E$  are the contributions of these different processes to the general disorientation.  $E$  is the permanent birefringence ratio. The fitting result is:  $C = 0.23$ ,  $D = 0.24$ ,  $E = 0.53$ ,  $t_1 = 17.74$ ,  $t_2 = 397.89$  and  $t_3 = 4481.07$ . The calculation result shows that there is about 73 % permanent refractive index preserved. It is to say that the permanent  $\Delta n$  is  $7 \times 10^{-4}$ , which ensures the stability of written grating. Moreover, the theoretical curve, fitting very well the experimental curve, indicates that the result is reasonable.

#### 4. Conclusions

A single mode photosensitivity POF with azobenzene copolymer as a core material has been made by a technique developed in our group. A 120  $\mu\text{m}$  long-period birefringence grating with a

50 % duty cycle has successfully written within the core of the fibre by amplitude mask technique. A cheaper 532 nm laser was used as writing beam instead much expensive excimer laser, so this fabrication method is promising for the mass production of fiber gratings. The grating obtained from this photoactive single mode POF is stable, and can be further used in optical fibre sensing and other wavelength tuning devices.

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### References

- [1] K. O. Hill, Y. Fujii, D. C. Johnson, B. S. Kawasaki, *Appl. Phys. Lett.* **3**, 647 (1978).
- [2] S. Y. Kim, S. B. Lee, S. W. Won, S. S. Choi, J. Jeong, *Electron Lett.* **34**, 104 (1998).
- [3] Z. Xiong, G. D. Peng, B. Wu, P. L. Chu, *IEEE Photonic Tech. L* **11**(3), 352 (1999).
- [4] H. Y. Liu, G. D. Chu, P. L. Chu, *IEEE Photonic Tech. L.* **13**(8), 824 (2001).
- [5] P. L. Chu, G. D. Peng, Z. Xiong, *Proc. 8<sup>th</sup> Int. POF Conf. '99*, July, 242 (1999).
- [6] M. G. Kuzk, U. C. Paek, C. W. Dirk, *Appl. Phys. Lett.* **59**(8), 902 (1991).
- [7] H. Kanbara, M. Asobe, K. Kubodera, T. Kaino, *Appl. Phys. Lett.*, **61**, 2290 (1992).
- [8] Z. Xiong, G. D. Peng, P. L. Chu, *Opt. Eng.* **39**(3), 624 (2000).
- [9] A. Tagaya, Y. Koike, E. Nihei, S. Teramoto, K. Fuji, T. Yamamoto, K. Sasaki, *Appl. Opt.* **34**, 988 (1995).
- [10] G. D. Peng, P. L. Chu, Z. Xiong, T. Whithead, R. P. Chaplin, *Opt. Commun.* **129**, 353 (1996).
- [11] H. Liang, Q. Zhang, Z. Q. Zheng, H. Ming, *Opt. Lett.* **29**(5), 477 (2004).
- [12] G. D. Peng, Z. Xiong, P. L. Chu, *Opt. Fiber Technol.* 242 (1999).
- [13] X. S. Xu, H. Ming, P. Wang, Z. C. Liang, Q. Zhang, *J. Opt. A: Pure Appl. Opt.* **4**, L5-L7 (2002).
- [14] G. D. Peng, P. L. Chu, in "Polymer Optical Fibers", Ed: Nari Singh Nalwa, American Scientific Publication, 57 (2004).
- [15] G. D. Peng, P. L. Chu, X. Lou, R. A. Chaplin, *J. Electr. Electron. Eng. Aust.*, 289 (1995).
- [16] X. S. Xu, H. Ming, Q. J. Zhang, *Opt Commun*, **204**, 137 (2002).
- [17] A. Natansohn, P. Rochon, *Chem. Rev.* **102**, 4739 (2002).
- [18] E. Snitzer, Cylindrical dielectric waveguide modes, in: *J. Opt. Soc. Am.* **51**, 491 (1961).
- [19] D. W. Garvey, K. Zimmerman, P. Young, J. Tostenrude, J. S. Townsend, M. Lobel, M. Dayton, R. Wittorf, M. G. Kuzyk, J. Sunick, C. W. Dirk, *J. Opt. Soc. Am. B* **13**, 2017 (1996).
- [20] M. G. Kuzyk, D. W. Garvey, B. K. Canfield, S. R. Vigil, D. J. Welker, J. Tostenrude, C. Breckon, *Chemical Physics* **245**, 327 (1999).
- [21] J. Zagari, A. Argyros, N. A. Issa, G. Barton, G. Henry, M.C.J. Large, L. Poladian, M. A. van Eijkelenborg, *Opt. Lett.* **29**(8), 818 (2004).
- [22] O. Hiroshi, K. Nozomu, K. Nobuhiro, *Optical materials* **15**, 33 (2000).