J. Opt. A: Pure Appl. Opt. **5** (2003) S92–S96 PII: S1464-4258(03)58397-0

Femtosecond laser irradiation of polymethylmethacrylate for refractive index gratings

P J Scully[1], D Jones[2] and D A Jaroszynski[2]

[1] Department of Instrumentation and Analytical Science, UMIST, PO Box 88, Manchester M60 1QD, UK
[2] Strathclyde Electron and Terahertz to Optical Pulse Source, University of Strathclyde, Department of Physics and Applied Physics, John Anderson Building, 107 Rottenrow, Glasgow G4 0NG, UK

Received 13 January 2003, in final form 11 April 2003
Published 25 June 2003
Online at stacks.iop.org/JOptA/5/S92

Abstract
Polymethylmethacrylate (PMMA) or Perspex is an inexpensive polymer widely used for making the cores of communications grade polymer optical fibres (POFs) and as a substrate for polymer optoelectronic devices and integrated waveguides. Periodic refractive index structures have been written in undoped PMMA using multiple pulses of 40 fs duration from a 1 kHz Ti:sapphire femtosecond laser operating at the fundamental (800 nm). A refractive index change (Δn) of $5 \pm 0.5 \times 10^{-4}$ was observed before the onset of striations. Optimization of writing conditions for refractive index modification of POF fibres or bulk undoped PMMA will enable structures such as Bragg gratings, long-period gratings, mode couplers, microlens arrays, and zone plates to be written.

Keywords: Polymethylmethacrylate, polymer optical fibre, refractive index, femtosecond laser

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Despite the current economic crisis in optical telecommunications leading to decreased demand for glass optical fibre, use of plastic optical fibre (POF) is rapidly expanding. The POF market for data communications is predicted to grow from \$500 million in 2002 to over \$2 billion in 2006 [1]. Applications will be split approximately as follows: 40% consumer electronics, 40% automotive, and others including interconnect, premises wiring, and industrial control.

POF has suffered from a poor image compared with glass silica fibre, but its cheapness, ease of termination, and robustness make it ideal for local area networks. In Europe and Japan, POF is extensively used for data communication in automobiles, and for home networking based on IEEE 1394. Single-mode and graded-index POF fibres are available, and Japanese-led advances in materials and manufacturing have increased the POF bandwidth to up to 10 Gbits s^{-1} and reduced losses down to 10 dB km^{-1} [2–4]. Bragg gratings have been written into doped POF [5, 6], and microstructured photonic POF fibres have been produced [7].

POF devices and sensors have several advantages over glass fibre (GF) and are listed as follows: POF is inexpensive, rugged, and does not suffer the problematic cleaving and poor coupling that are associated with GF. The drawing process is at low temperature, so organic chromophores and rare-earth organic metallics, that would be destroyed by the high temperatures used in GF production, can be added to POF. Fibre Bragg gratings in POF have advantages over GF gratings because the bulk thermo-optic, electro-optic, and strain sensitivities of polymer are up to ten times those of glass, enabling cheaper light sources and spectral measurement systems to be used. Evanescent POF sensors, using multimode large-diameter fibre, are an order of magnitude more sensitive than multimode evanescent GF sensors [8, 9]. POF is tougher, requiring less local reinforcement when embedded into a material, hence making it more sensitive to the intrinsic local strain of the material, and it is easier to terminate and couple

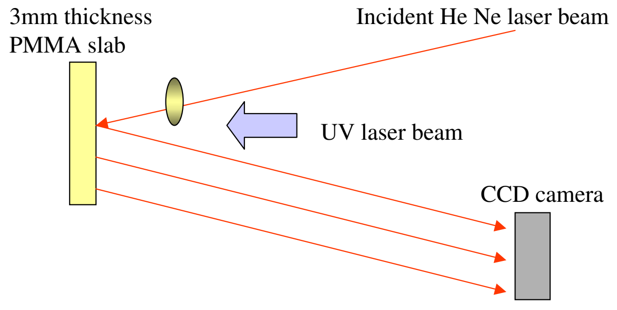

Figure 1. The experimental configuration for measuring the fringe shift. The reflected fringes are imaged onto a CCD camera.

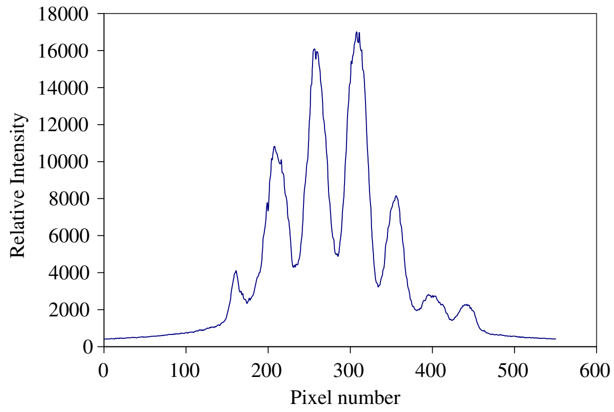

Figure 2. A cross-section of Fabry–Perot fringes produced by illumination of a PMMA slab with a HeNe laser, and imaged onto a Princeton Instruments liquid-nitrogen-cooled CCD camera.

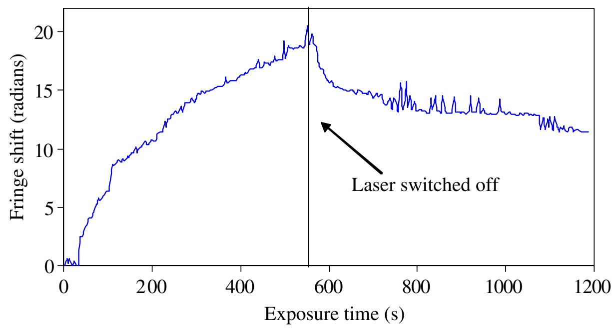

Figure 3. The shift of the interference fringes when the PMMA slab was irradiated at 248 nm. Fluence: 26 mJ cm^{-2}; 1847 pulses; 5 Hz.

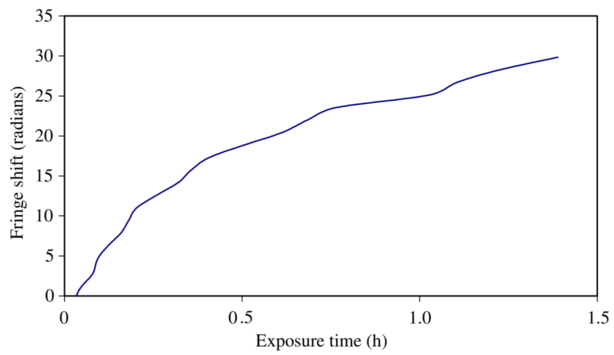

Figure 4. The shift of the interference fringe when the PMMA slab was irradiated at 216 nm. Fluence: 1 mJ cm^{-2}; 50 000 pulses; 10 Hz.

to detectors and emitters. Microstructured POF is lower cost, more rugged, and easier to manufacture than glass photonic crystal fibres [7].

A number of studies of pre-ablation and UV laser-photoinduced refractive index modification of pure polymethylmethacrylate (PMMA) thin films were made at single UV laser wavelengths that have been used for photomodification of glass—for example: KrF excimer radiation at 193 nm [10]; argon-ion laser radiation at 351/363 nm [11]; 216 nm (the fifth harmonic of the Nd:YAP laser) [12]; 248 nm [13]; broadband UV sources [14]. Recently, a study was performed at excimer wavelengths of 193, 248, and 308 nm, in which the photochemical modification of irradiated PMMA was investigated using QMS, XPS, and FTIR techniques [15].

A range of UV wavelengths (363, 351, 308, 266, 240, 237.5, 230, 220, and 216 nm) were investigated to create photoinduced refractive index changes in bulk PMMA material [16]. Changes in optical path length were measured using a 3 mm thick PMMA slab as a Fabry–Perot etalon (figure 1). When the UV irradiated area was illuminated with a HeNe laser, shifts in reflected interference fringes (figure 2) were observed using a CCD camera, indicating changes in sample thickness, refractive index, and penetration depth in agreement with other researchers' findings [10, 12]. Periodic refractive index changes of about 1% were induced in PMMA slabs at 216 nm (figure 3) and 248 nm (figure 4), but the penetration exhibited exponential decay and was limited to a depth of 10–100 μm. In addition, exposure at the appropriate fluence took upto 1 h. Commercially available POF with a pure PMMA core is of large diameter (0.98 mm diameter), while single-mode POF was unavailable, so in order to measure the effect of laser-induced refractive index changes in the fibre, it was tapered to 100 μm and the far-field modal distribution was monitored as a function of laser irradiation [17]. The UV wavelengths were generated using: a Lumonics Pulsemaster Excimer laser emitting at 308 nm, pumping a Lambda Physik SL3002 dye laser and SHG; and a Spectra Physics GCR-170 Nd:YAG laser emitting at 335 nm and pumping a Lambda Physik LAS20505 dye laser and SHG.

The problem with UV irradiation of PMMA is that the absorption band restricts penetration of the UV light to a depth of 10–100 μm. Researchers have tried to combat this by doping PMMA with organic dyes to enhance its photosensitivity to near-UV and visible laser light. For example, PMMA doped with 4-nitrophenyl-N-butylnitrone and illuminated with 330 nm UV light [18] achieved a 2% refractive index change after 60 s. PMMA thin films were doped with benzoquinone to enable volume gratings to be written at blue and green wavelengths [19]. Refractive index modification of polymer fibres has been limited to doped material employing UV lasers to alter the refractive index of the material [5, 6]. Refractive index changes (Δn) of between 3.3×10^{-5} and 1×10^{-4} have been observed in fibre doped with fluorescein or monomers. Unfortunately, doping the material is both expensive and time consuming. On the other hand, PMMA or Perspex is an inexpensive polymer widely used for making the cores of communications

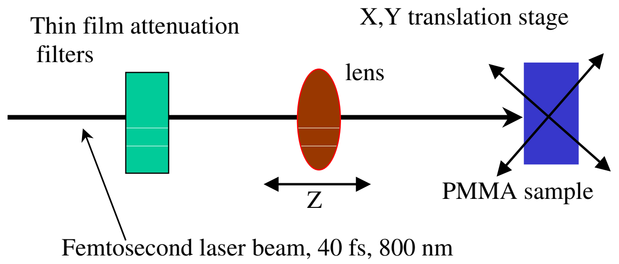

Figure 5. A schematic diagram of the femtosecond laser experimental system.

grade polymer optical fibres (POFs) and as a substrate for polymer optoelectronic devices and integrated waveguides. The optimization of writing conditions for refractive index modification of POF fibres or bulk undoped PMMA would allow structures such as Bragg gratings, long-period gratings, mode couplers, microlens arrays, and zone plates to be written into a material that is widely available and inexpensive.

The goal of this present work is to examine whether it is possible to suitably modify the refractive index of undoped PMMA using femtosecond laser radiation. The absorption of femtosecond laser radiation by materials that are transparent to the fundamental wavelength is possible through multiphoton ionization to create free electrons. Impact ionization of bound electrons by free electrons accelerated in the laser field results in an avalanche process generating an exponential rise in the free electron density. Above a critical free electron density ($\sim 10^{18}$–10^{21} electrons cm^{-3}) significant optical absorption occurs leading to irreversible modification of the media. With the laser suitably focused into the material the intensity at the focus will be sufficiently high for absorption to occur via multiphoton ionization. Consequently, it is possible using a femtosecond source to discretely alter the refractive index inside bulk transparent optical media provided that the absorption of the incident radiation suitably modifies the composition of the material. Initial work in femtosecond laser refractive index modification of inorganic glasses dates from 1996. Three-dimensional arrays of bits were written into optical materials for optical storage and retrieval, and substantial refractive index modification was observed in undoped glasses [20, 21] with Δn of 0.05% achieved. Japanese researchers demonstrated waveguides and gratings written in various inorganic glasses [22–24] with Δn of up to 3%. In 2001, US researchers demonstrated single-mode X-couplers and three-dimensional waveguides in glasses with refractive index changes up to 1% [25], and Japanese researchers reported holographic refractive index gratings with $\Delta n \approx 3 \times 10^{-4}$ in bulk azo-dye-doped PMMA produced using a femtosecond laser [26, 27]. In 2002, the same researchers reported gratings structures in acrylate block co-polymers, with $\Delta n \approx 3 \times 10^{-3}$–$2 \times 10^{-4}$ [28]. Most recently (October 2002), single-femtosecond-pulse holography in undoped PMMA was reported [29].

2. Experimental details

The experiments were performed using a Thales Alpha 1000 laser, producing pulses of 40 fs duration at a wavelength of 800 nm. A schematic diagram of the experimental system is

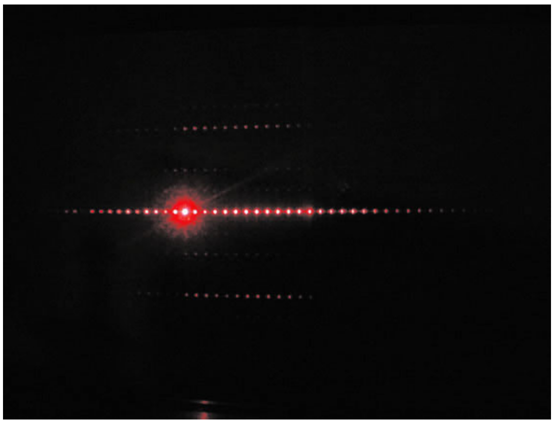

Figure 6. The far-field diffraction pattern from a refractive index grating written in Perspex showing 22 diffraction orders.

shown in figure 5. Light from the femtosecond laser beam was focused into 3 mm thick Perspex slabs of dimensions 15×15 mm, using a simple 80 mm focal length lens (F-No: 10) mounted on a manual translation stage. The femtosecond laser power was attenuated using an array of neutral density filters to control the power densities incident on the PMMA sample over the range 0.03–1 J cm^{-2}. The Perspex sample was mounted on an x–y translation stage and gratings were written by moving the slab relative to the stationary femtosecond laser beam, using an x–y translation stage interfaced to a computer. The grating spacing was determined using Labview virtual instrument software to control the x- and y-positioning of the sample relative to the beam. Thus the grating line spacing (d), number of lines (n), and size of the grating structure could be precisely controlled. The laser power that the sample was exposed to was controlled by the x- and y-velocities of the translation stage.

A 2 mW HeNe laser was incident normally on the written grating and formed an impressive far-field diffraction pattern with 22 orders as shown in figure 6. The fraction of incident HeNe light intensity diffracted into the first order was measured using a silicon detector mounted on a translation stage to form a measure of the diffraction efficiency, η.

The magnitude of the refractive index modification (Δn) can be determined from the diffraction efficiency using equation (1) [30]. Here θ is the incident angle from the normal in the media, η the diffraction fraction into the first order and h the depth of the refractive index modification. We have

$$\Delta n = \frac{\lambda \cos(\theta) a \tanh(\sqrt{\eta})}{\pi h}. \tag{1}$$

A range of incident femtosecond laser intensities from 0.03 to 1 J cm^{-2} were used to write gratings into different PMMA slabs using identical writing conditions such as the writing velocities in the x- and y-directions, grating line spacing (d), and number of lines (n). Each grating was identical apart from the refractive index change induced by the laser fluence. For each grating, the HeNe laser power diffracted into the first order of diffraction, η was measured. The diffraction efficiency was plotted versus the incident femtosecond laser intensity as shown in figure 7. Each of the 18 points on the plot is measured from a separate grating written at a specified laser fluence.

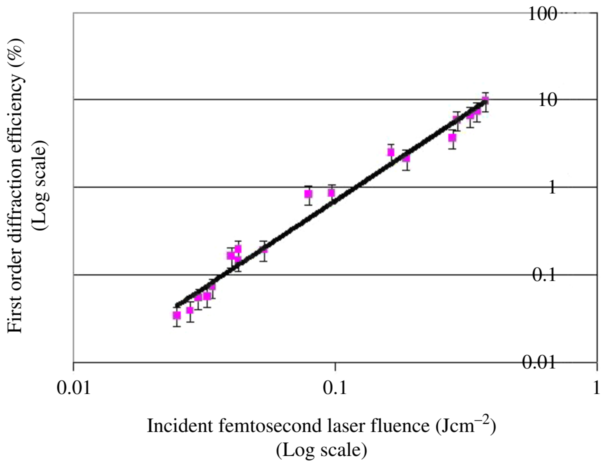

Figure 7. The first-order diffraction efficiency of a refractive index grating as a function of the incident femtosecond laser fluence. The grating was written at a position 0.5 mm into the material.

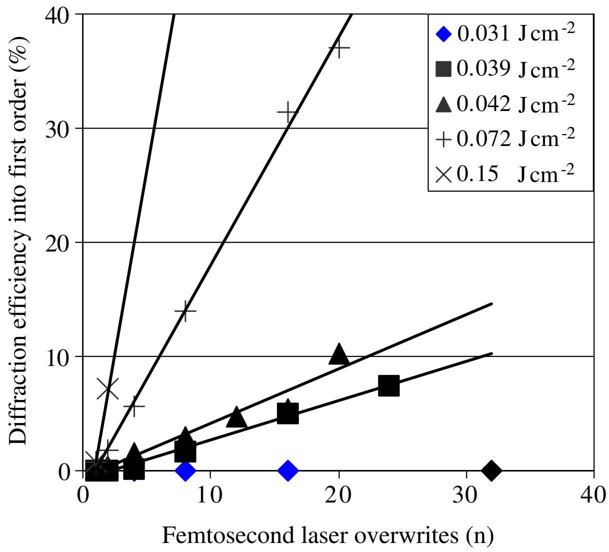

Figure 8. The first-order diffraction efficiency of refractive index gratings ($d = 80$ μm) as a function of the incident femtosecond laser fluence for various overwrites. The gratings were written at a position 0.5 mm into the material. Incident fluence, in ascending order: 0.031, 0.039, 0.042, 0.072, and 0.15 J cm^{-2}.

3. Results and discussion

A range of refractive index gratings were written at various spacings ($d = 20$, 40, and 80 μm), at a depth of 0.5 mm below the surface in undoped PMMA slabs, using a range of laser fluences from 0.03 to 1 J cm^{-2}.

The refractive index structures have sufficient contrast to be observable using an optical microscope, and diffract white light. When illuminated normally with a HeNe laser, the gratings produce a highly ordered far-field diffraction pattern from a refractive index grating, as shown in figure 6.

Equation (1) indicates that the induced refractive index change, Δn, can be related to the diffraction efficiency, η. The angle of incidence from the normal, θ, is 0°, since the HeNe laser is incident normally on the grating. To determine the depth (h) of the refractive index modification, samples were cut with cross-sections through the grating and the surfaces polished. The refractive index modification depth (h) could then be viewed and measured using an optical microscope. The depth of the refractive index structure was measured as 200 ± 20 μm. Inserting this value into equation (1) for the diffraction fraction obtained, 0.25 into the first order, gives a maximum refractive index modification (Δn) of $5 \pm 0.5 \times 10^{-4}$.

Since diffraction efficiency is proportional to refractive index modulation, the increase in magnitude of the refractive index modification as a function of laser fluence is shown in figure 7. A power fit to the data set of figure 7 returns a power of 1.99. This indicates that absorption occurs at the second harmonic (at a wavelength of 400 nm)—in other words, two photons of wavelength 800 nm are required. A threshold femtosecond laser fluence of $\sim$0.03 J cm^{-2} to initiate diffraction into the first order, and thus refractive index modification, is observed in figure 7. Below this fluence level no diffraction is observed, indicating that refractive index modification of the material is not achieved even when overwritten up to 30 times as shown in figure 8. In figure 7, above an incident fluence level of $\sim$0.8 J cm^{-2}, machining and damage/filament formation take place, resulting in scatter and a resultant decrease in the diffraction efficiency.

Gratings were overwritten up to 32 times using a range of incident laser fluences at 0.031, 0.039, 0.042, 0.072 and 0.15 J cm^{-2}. The efficiency of diffraction into the first order is plotted versus number of overwrites for each laser fluence to form a number of plots on the same graph in figure 8. Observation of multiple overwrites indicates that refractive index modification is a cumulative process; this is clearly evident in figure 8. Furthermore, when overwriting, a cumulative incident fluence level ceiling of $\sim$0.8 J cm^{-2} is still observed, above which damage/filament formation takes place.

The efficiency of refractive index modification at different depths within the PMMA material was investigated and no limitations or dependences are observed to a depth of 15 mm. Furthermore, moving the focus position through the PMMA material enabled ‘thick’ gratings to be produced. One point of note was the lack of ability to modify the refractive index of PMMA at the surface. In all cases either no modification occurred or on increasing the incident laser fluence damage/filamentation was observed. To overcome this, two PMMA samples were compressed together and the focus positioned on the interface; refractive index modification was then observed at the surfaces of both samples.

4. Conclusions and future work

Periodic refractive index structures were successfully written in bulk undoped PMMA using a femtosecond laser. The measured refractive index change (Δn) of 5×10^{-4} is greater than that achieved in doped PMMA using UV lasers [5, 6]. Doping the material is both expensive and time consuming; however, undoped PMMA is an inexpensive polymer widely used for making the cores of communications grade POFs and polymer optoelectronic devices. Thus the ability to modify the refractive index of undoped PMMA will allow structures such as Bragg gratings, mode couplers, microlens arrays, and zone plates to be written into a material that is widely available and inexpensive. The utilization of femtosecond lasers to write Bragg structures into materials also overcomes the penetration limitation associated with UV lasers. The femtosecond laser is able to discretely modify the refractive index at any required point within the material—not just at the surface.

Currently, the long-term temperature stability of the photoinduced gratings is under investigation, while UV–visible and FT infrared spectroscopic studies are being employed to elucidate the material modification mechanism.

Acknowledgments

We thank the EPSRC and SHEFC for continued support and Liverpool John Moores University Research Fund for a Travel Fellowship for Patricia Scully. Grateful acknowledgement is made to Enrico Brunetti for writing the Labview programs that control the translation stages and David Clark for preparation of experimental equipment.

References

[1] *POF Market and Technology Assessment* 2002 (Boston, MA: IGI Consulting Group Inc.)

[2] Koike Y and Ishigure T 1999 Bandwidth and transmission distance achieved by POF *IEICE Trans. C Electron.* **E82-C** 1553–61 http://search.ieice.org/1999/e82-c_8_1553.pdf

[3] Koike Y, Ishigure T, Satoh M and Nihei E 1998 High-speed photonics polymer and its application *Pure Appl. Opt.* **7** 201–10

[4] Giaretta G, White W, Wegmuller M and Onishi T 2000 High-speed (11 Gbit s^{-1}) data transmission using perfluorinated graded-index polymer optical fibers for short interconnects ($<$100 m) *IEEE Photonics Technol. Lett.* **12** 347–9

[5] Peng G D, Xiong Z and Chu P L 1999 Photosensitivity and gratings in dye-doped polymer optical fibres *Opt. Fiber Technol.* **5** 242–51

[6] Xiong Z, Peng G D, Wu B and Chu P L 1999 Highly tunable Bragg gratings in single mode polymer optical fibres *IEEE Photonics Technol. Lett.* **11** 352–4

[7] Eijkelenborg M V, Large M, Argyros A, Zagari J, Manos S, Issa N A, Bassett I M, Fleming S C, McPhedran R C, Martijn de Sterke C and Nicorovici N A P 2001 Microstructured polymer optical fibre *Opt. Express* **9** 319–27

[8] Bartlett R J, Philip-Chandy R, Eldridge P, Merchant D F, Morgan R and Scully P J 2000 Plastic optical fibre sensors and devices *Trans. Inst. Meas. Control* **22** 431–57

[9] Chandy R P, Scully P J, Eldridge P, Grapin G, Jonca G, D'Ambrosio G and Colin F 2000 An optical fibre sensor for biofilm measurement using intensity modulation and image analysis *IEEE J. Sel. Top. Quantum Electron.* **6** 764–72

[10] Baker A K and Dyer P E 1993 Refractive index modification of polymethylmethacrylate (PMMA) thin films by KrF-laser irradiation *Appl. Phys.* A **57** 543–4

[11] Bozhevolnyl S I and Potemkim I V 1994 Dynamics of ablation of polymethylmethacrylate films by near ultraviolet light of a Ar^+ laser *J. Phys. D: Appl. Phys.* **27** 19–24

[12] Bityurin N, Muraviov S, Alexandrov A and Malyshev A 1997 UV laser modifications and etching of polymer films (PMMA) below the ablation threshold *Appl. Surf. Sci.* **109** 270–4

[13] Kuper S and Stuke M 1989 UV excimer laser ablation of PMMA at 248 nm: characterisation of incubation sites with Fourier transform IR and UV spectroscopy *Appl. Phys.* A **49** 211–15

[14] Frank W B 1998 Passive components in plastic materials using surface modification by ionizing radiation *7th Int. Plastic Fibres Conf. '98 (Berlin, Oct. 1998)* (Basel: AKM) pp 273–86

[15] Wochnowski C, Metev S and Sepold G 2000 UV-laser assisted modification of the optical properties of polymethylmethacrylate *Appl. Surf. Sci.* **154** 706–11

[16] Scully P J, Caulder S and Bartlett R 2000 UV-laser photo-induced refractive index changes in poly methyl methacrylate and plastic optical fibres for application as sensors and devices *The Central Laser Facility Annual Report 1999–2000* pp 145–7 http://www.clf.rl.ac.uk/Report/1999-2000/Contents.htm

[17] Scully P J, Bartlett R, Caulder S, Eldridge P, Chandy R, McTavish J, Alexiou V, Clarke I P, Towrie M and Parker A W 2000 UV laser photo-induced refractive index changes in poly-methyl-meth-acrylate and plastic optical fibres for application as sensors and devices *OFS2000: 14th Int. Conf. on Optical Fibre Sensors (Oct. 2000)* (Florence: CRN) pp 854–7

[18] Miyata S, Kim J-C, Obara A, Kada T and Watanbe T 1997 Novel refractive index control methods for polymers *Proc. POF Conf. '97 (Hawaii, Sept. 1997)* (Yokohama: POF Consortium) pp 37–8

[19] Kumar J, Li L, Chittibabu K G, Kumar N, Kim D Y, Jiang X L and Tripathy S 1997 Surface and volume gratings in polymer waveguides and optical fibres *Proc. POF Conf. '97 (Hawaii, Sept. 1997)* (Yokohama: POF Consortium) pp 88–9

[20] Glezer E N, Milosavljevic M, Huang L, Finlay R J, Her T-H, Callan J P and Mazur E 1996 Three dimensional optical storage inside transparent materials *Opt. Lett.* **21** 2023–5

[21] Efimov O M, Glebov L B, Richardson K A, Van Stryland E, Cardinal T, Park S H, Couzi M and Brunéel J L 2001 Waveguide writing in chalcogenide glasses by a train of femtosecond laser pulses *Opt. Mater.* **17** 379–86

[22] Davies K M, Miura K, Sugimoto N and Hirao K 1996 Writing waveguides in glass with a femtosecond laser *Opt. Lett.* **21** 1729–31

[23] Hirao K and Miura K 1998 Writing waveguides and gratings in silica and related materials by a femtosecond laser *J. Non-Cryst. Solids* **239** 91–5

[24] Miura K, Inouye H, Qiu J, Mitsuyu T and Hirao K 1998 Optical waveguides induced in inorganic glasses by a femtosecond laser *Nucl. Instrum. Methods Phys. Res.* B **41** 726–32

[25] Minoshima K, Kowalevicz A M, Hartl I, Ippen E P and Fujimoto J G 2001 Photonic device fabrication in glass by use of nonlinear materials processing with a femtosecond laser oscillator *Opt. Lett.* **26** 1516–18

[26] Si J, Qiu J, Zhai J, Shen Y and Hirao K 2002 Photoinduced permanent gratings inside bulk azodye-doped polymers by the coherent field of a femtosecond laser *Appl. Phys. Lett.* **80** 359–61

[27] Zhai J F, Shen Z Q, Si J H, Qiu J R and Hirao K 2001 The fabrication of permanent holographic gratings in bulk polymer medium by a femtosecond laser *J. Phys. D: Appl. Phys.* **34** 3466–9

[28] Katayama S, Horrike M, Hirao K and Tsutsumi N 2002 Diffraction measurement of grating structure induced by irradiation of femtosecond laser pulse in acrylate block copolymers *Japan. J. Appl. Phys.* 1 **41** 2155–62

[29] Li Y, Yamada K, Ishizuka T, Watanbe W, Itoh K and Zhou Z 2002 Single femtosecond pulse holography using polymethylmethacrylate *Opt. Express* **10** 1173–8

[30] Mailis S, Anderson A A, Barrington S J, Brocklesby W S, Greef R, Rutt H N, Eason R W, Vainos N and Grivas C 1998 Photosensitivity of lead germanate glass waveguides grown by pulsed laser deposition *Opt. Lett.* **23** 1751–3