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# Influence of chemical polymer composition on integrated waveguide formation induced by excimer laser surface irradiation

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ABSTRACT

We show that the chemical composition and the amount of residual monomers in polymethylmethacrylate significantly affect the evolution of optical waveguide formation induced by UV surface irradiation. We employ an interferometric approach in Mach-Zehnder configuration to determine the refractive index depth profile in different planar polymethylmethacrylate materials. Our results reveal a distinctive different surface and buried waveguide formation for materials having different monomer content. In particular, we find that for smaller residual monomer content buried waveguide formation is less pronounced, which is in turn preferential for a selective light guidance in planar polymer structures. Attenuation measurements confirm a difference in attenuation coefficient of 0.5 dB/cm.



## 1. Introduction

Polymer optical waveguides recently attract considerable interest in telecommunication and sensor systems. Beside polymer optical fibers (POF), planar polymer optical substrates offer the unique possibility to realize optical integrated circuits (OIC). The waveguides in which can be formed by either conventional lithographic techniques, embossing and imprint technologies or direct writing using UV radiation [1–4]. For the later process a detailed knowledge of the UV induced refractive index modification and its dependencies on irradiation parameters is indispensable as it determines the waveguide properties such as mode field distribution and attenuation.

Especially polymethylmethacrylate (PMMA) is a suitable and well explored material for polymer optical devices. Particularly, the possibility to alter the refractive index (RI) by UV irradiation well below 300 nm facilitates the generation of passive optical components and OIC [5–9]. The underlying complex photochemical processes of this UV induced modification have been studied in [10–13] comprising competing processes such as UV induced direct photopolymerisation, main chain scission and side chain cleavage, respectively. Various studies have shown that these processes in PMMA lead to a refractive index modification that yields a surface waveguide as well as a buried waveguide [15–17]. However, previous studies focused on one PMMA material only and a difference of the material composition and particularly of the content of residual monomers have, though being repeatedly reported relevant in the underlying processes, to the best of our knowledge, not been studied so far.

In this contribution, we report on the UV excimer laser induced refractive index modification in different PMMA with varying composition. In particular, we study commercially available PMMA samples with different amount of copolymers and residual monomers. The refractive index profile has been measured by phase shifting interferometry in a Mach-Zehnder configuration as described by Shams El-Din et al. [17]. Compared to the research of Shams El-Din et al. who investigated refractive index depth profiles for one special polymethylmethacrylate material only, our results reveal that the generation of buried waveguides is significantly reduced for PMMA with a smaller amount of residual monomers.

## 2. Experimental

### 2.1. Materials

To investigate the influence of the chemical composition of polymethylmethacrylate on the UV induced optical waveguide

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formation, we studied two different commercially available PMMA grades, namely normal PMMA grade – subsequently referred to as standard PMMA – and impact-resistant PMMA grade (both by Goodfellow). According to the supplier, the latter is modified by an unspecified elastomer copolymer to enhance the impact resistance.

The spectral dependence of the absorption is determined by carrying out transmission and reflection measurements using a spectro-radiometer equipped with an integration sphere (Instrument Systems, transmission ($T$) measurement accuracy $\Delta T = \pm 0.1\%$). In addition, dispersion characteristics of both materials are measured by multi-wavelength refractometry using a white light Abbe refractometer (Atago DR-M2/1550, refractive index ($n$) measurement accuracy $\Delta n = \pm 0.0001$).

The chemical composition of the PMMA, in particular the content of residual monomers, i.e. methylmethacrylate (MMA), and the content of possible copolymers are determined by employing $^1$H NMR spectroscopy using a 400 MHz Bruker Avance DRX 400 NMR spectrometer. For these measurements, samples were prepared by dissolving 20 mg of each polymer type in chloroform. Standard PMMA needed a longer time for complete dissolution as compared to impact-resistant PMMA already indicating a different composition. The NMR spectrometer was calibrated by internal standard tetramethylsilane (TMS, chemical shift $\delta = 0$ ppm). The residual monomer content was determined by evaluating the signals at 6.10 ppm and 5.55 ppm resulting from the two hydrogen atoms at the $=CH_2$ double bond of residual MMA and comparing these to the ester signal of the entire polymer body which appears around 3.60 ppm ($-CH_3$ group, detected signal range from 3.39 to 3.85 ppm). Eq. (1) was applied to calculate the fractional residual MMA content by the use of integrated relative intensities of the relevant signals [14].

$$\%\mathrm{MMA} = \frac{(A_{6.1\,\mathrm{ppm}} + A_{5.55\,\mathrm{ppm}})/2}{(A_{3.39-3.85\,\mathrm{ppm}})/3} \quad (1)$$

### 2.2. Mach-Zehnder interferometer for refractive index profiles

In order to determine UV induced refractive index alterations at the irradiated surface a Mach-Zehnder interference microscope is employed. Fig. 1 shows the setup of the Mach-Zehnder measurement system based on the pioneering work by Shams El-Din et al. [15–17].

The beam of a HeNe laser ($\lambda = 632.8$ nm) is expanded by a 10× telescope allowing complete illumination of the relevant area on the sample. The widened beam is split into object and reference beam by beam splitter $BS_1$. The object beam travels through the sample waveguide area which alters the phase of the object beam relative to that of the reference beam. This results in a bend of the interference fringes according to the refractive index distribution. The sample is placed inside an optical glass cuvette filled with an immersion liquid matching the refractive index of the unilluminated PMMA substrates. This immersion oil with known refractive index serves as reference for the measured phase values and provides continuous interference fringes. Furthermore, by this approach only the shift of interference fringes due to the waveguide is visible. Two 10x microscope objectives (MO) with NA = 0.25 enlarge the beams such that $MO_1$ magnifies the viewed waveguide area and $MO_2$ equalizes the wavefront of object and reference beam. The resulting interferogram at the interferometer output is recorded by a monochromatic CCD camera (Allied Vision Marlin). In order to calculate refractive index values, the determination of phase difference values between object and reference arm out of the interferogram are necessary. For this purpose, Phase Shifting Interferometry (PSI) as a common approach for direct determination of phase values is applied. To facilitate this, mirror $M_2$ in the reference arm of the interferometer is mounted on a piezoelectric transducer (PZT) enabling an accurate phase shift of the reference beam. The phase is shifted 5 times by steps of 90° whereas an interferogram for each step is recorded. From these 5 different intensity values at each pixel the wrapped phase differences are calculated by the software Fringe Processor from BIAS GmbH (Fig. 2a) After unwrapping (Fig. 2b) and normalization (Fig. 2c) the phase values are converted into refractive index values. For better visualization of the UV-modified PMMA area the obtained phase map can be displayed as a 3D plot (Fig. 2d).

Integrated waveguides in PMMA substrate are usually written by irradiating the planar surface with a KrF excimer laser at 248 nm. However, for the measurement of the refractive index depth profile with the Mach-Zehnder interferometer the waveguides are generated in an optically polished edge of the PMMA substrate. This approach shortens the optical path length of the lateral measurement beam through the PMMA samples, which enables the use of interferometry and allows the application of the multi-layer waveguide model according to [15]. The waveguide is written using an amplitude mask (width 150 μm) in contact exposure mode. According to our previous work on polymer waveguides in PMMA, waveguides are written using the following excimer laser parameters: exposure 8 mJ/cm$^2$ and pulse frequency 200 Hz [8]. The number of pulses has been varied between 1000 and 8000 shots. To increase the speed of the light induced chemical reactions and to stabilize the refractive index modification, the samples are tempered for 12 h at 60 °C after UV illumination. Afterwards,

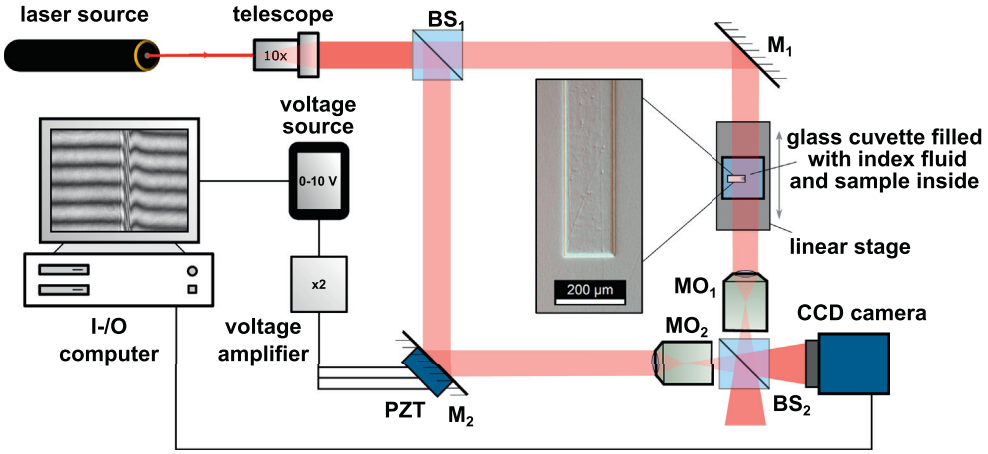


**Fig. 1.** Mach-Zehnder interference microscope setup for measurement of refractive index depth profiles of UV illuminated polymer samples. A microscope image shows the UV modified polymer sample area.