2536

UV written waveguides using crosslinkable PMMA-based copolymers

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New crosslinkable copolymers poly(methylmethacrylate/2-methacryloylethylmethacrylate) (P(MMA/MAOEMA)) were developed for waveguide applications. P(MMA/MAOEMA) can crosslink under either UV exposure or heating. The UV induced refractive index change in unreacted P(MMA/MAOEMA) is found to depend on the fluence. UV exposure of thermally crosslinked P(MMA/MAOEMA) can induce further structure change and thus index change, and therefore, was found to be useful for creating the core layers in optical waveguides. The photosensitivity of the thermally crosslinked polymers sufficient for the fabrication of low loss (<1dB/cm) channel waveguides in the thermally crosslinked copolymer system.

Introduction

The expansion of high capacity optical transmission techniques into highly price-sensitive areas such as datacomms and access networks requires a major reduction in the cost of optical components. The implementation of integrated optics is one of the most promising approaches to achieve this cost reduction, by incorporating many optical functions onto the same planar chip. However, although integrated optical planar devices look increasingly attractive, the complexity of their fabrication in conventional glass and crystal materials is likely to prevent their use for the most cost sensitive applications. Polymer waveguides are potentially very simple to process and are promising for low cost devices[1-3].

However, the attractions of polymer integrated optics are only beginning to come true in real-world devices. Further development and characterization of suitable polymeric materials is needed. In addition, the fabrication techniques for polymeric waveguides and for their integration with glass optical fibers should be also developed.

The key requirements imposed for such materials are low transmission losses (<0.5 dB/cm), and sufficient thermal and environmental stability to withstand typical IC processing and operating conditions. The properties of a variety of polymers have been studied previously[4-14]. Most of the early work concentrated on the use of poly(methyl methacrylate) (PMMA) as a waveguide material, because of its well-known optical properties and good film forming behaviours[1-3].

The PMMA based polymers described in the present work are self-crosslinkable by UV exposure as well as by heating. In order to be able to modify easily the refractive index in these systems, we have prepared copolymers of hydroxyethylmethacrylate (HEMA) and methylmethacrylate (MMA) and have introduced crosslinkable sites onto the hydroxyethyl side chains to afford poly(methylmethacrylate/2-methacryloyl ethylmethacrylate) (P(MMA/MAOEMA)). Whilst three- and four- and five-component polymer systems incorporating several functional esters attached to a methacrylate-based core have previously been described for use in lithographic systems (Kodak Patent[15]) the application of co-polymers of the type reported here for wave-guide applications is novel.

Conventionally polymer channel waveguides are fabricated using photolithographic techniques. However a direct UV-witing technique[12] has recently been used since it is much simpler for the fabrication of complex devices. We have used such UV writing techniques to create channel waveguides in this paper.

For the waveguide fabrication to be successful a suitable polymer crosslinking and degradation temperatures are important for making the core and cladding layers. Therefore, in this work considerable attention has been paid to thermal stability. For the direct UV writing technique it is essential for us to understand how the photosensitivity (refractive index change) and thickness depend upon laser exposure.

In this report the thermal properties, photosensitivity, thickness change and crosslinking characteristics of the polymers are described. We have used solid state NMR to investigate the processes occurring when thermally pre-crosslinked polymers are exposed to UV radiation. The small spot sizes used in the direct UV-writing of waveguides result in very high peak powers; these, in turn, can result in a number of different waveguide morphologies depending on laser power and fluence. SEM images of actual waveguide structures are presented to show these effects. We have also investigated on waveguide loss in devices fabricated from these thermally crosslinked polymers. Finally we discuss the potential of our system.

In this work it is important to establish whether or not the P(MMA/MAOEMA) has been thermally crosslinked. Consequently we shall adopt the term "raw P(MMA/MAOEMA)" to indicate that thermal crosslinking has not been carried out.

Fabrication

Polymer synthesis

The poly (methylmethacrylate/methacryloylethylmethacrylate) (P(MMA/MAOEMA)) system was developed specifically for waveguide applications. It has a number of attractive features, in particular, the flexibility to control the overall refractive index by altering the feed monomer ratios, and the ability to introduce the methacryloyl group as a cross linkable site. In these studies we have prepared copolymers using a wide range of monomer feed ratios of MMA to HEMA (0, 10, 20, 34, 47, 70, 85, and 100% HEMA-content copolymers) to build up information on the range of achievable refractive indices. The detailed preparation and chemical properties of these polymers will be the subject of an additional paper[16], but a brief description is provided below. The synthetic route is summarized in scheme 1.
Scheme 1.

The first step involves thermally initiated free-radical polymerization of the monomers using AIBN (azoisobutyronitrile). Polymerization was carried out at 60°C and the resulting polymers were precipitated into ether. The reproducibility of the copolymer composition was excellent[16].

In general, esterification of an alcohol is performed in the presence of an organic base and a solvent[17]; in the present case Et_3N (triethylamine) and DCM (dichloromethane) were used for this purpose. Methacrylic anhydride (MAAN) was used as an acylating agent since this anhydride is suitable for the preparation of esters when mild conditions are required. The esterification was successful and in most cases a pure white powder was obtained. In the present study a 47% HEMA content P(MMA/MAOEMA) was used as the standard material unless otherwise specified.

Polymer film preparation

Polymers were dissolved either in PGMEA (propyleneglycol methyl ether acetate) or in a cosolvent of PGMEA and MEK (methyl ethyl ketone). These solvents were purchased as spectroscopic grade from Aldrich and used without further purification.

The solutions were filtered through a 0.2 μm PTFE membrane filter and were spin-coated (at 1,000 ~ 4,000 rpm, using a spin-coater from Headway Research) either onto silicon or silica substrates. The film thickness was controlled by adjusting the solution concentration from 10 to 40 wt% and the spin speed. The spin-coated films were dried at 90°C in an oven for 5 min to remove residual solvent.

Film thickness was measured by using an α-step from Tencor Instruments, a Jobin Yvon ellipsometer, and a manual prism coupler.

Waveguide fabrication and testing

To fabricate the layers for making optical waveguides a solution containing 25% polymer by weight (47% HEMA content P(MMA/MAOEMA)) was spin-coated on a 50 mm diameter silica substrate and then thermally crosslinked (2 h at 140°C). The film thickness was ~4μm.

The channel waveguides were written using a frequency-doubled argon ion laser (244nm). The beam from the laser was brought to a tight focus in the polymer core layer. The substrate and layer was translated on air-bearing stages under computer control to define the waveguides – the system being capable sub-micron positional control.

The laser power was varied between 0.001 and 0.01W with a spot size of ~10 μm diameter. Multiple tracks were written with different scan speeds (0.80 - 0.14 mm/sec). Another cladding layer was then spin-coated with the same thickness as the first one on top of the core layer and thermally crosslinked (2 h at 140°C). Final preparation involved dicing and end-polishing of the waveguides for end-fibre launching.

It is important to distinguish between the irradiance or power density of a UV writing beam (expressed in this paper in units of W/mm^2) and the fluence which is the integrated energy per area (units of J/mm^2). As we will show later, the high laser powers available from our system mean that waveguides with the same fluence, but different writing powers can have very different characteristics.

For waveguide loss measurements, the light from a fiber-coupled He-Ne laser was launched into the waveguide by bringing the waveguide into close contact with the fiber. The waveguide propagation loss was obtained by using the cut-back method.

Results and Discussion

Thermal Properties

Waveguide materials need to have good thermal stability to withstand severe fabrication conditions as well as a potentially hostile operating environment. In our waveguide fabrication process, our raw polymer is thermally crosslinked at a high temperature (around 140°C). Consequently, we have determined a suitable crosslinking temperature for each copolymer depending on its composition and have also investigated the degradation temperature of our thermally crosslinked P(MMA/MAOEMA).

The thermal stability of the raw polymers studied by using a Perkin Elmer DSC (differential scanning calorimeter). The DSC curve for 70% HEMA content polymer is shown in figure 1. All the traces show a sudden drop in heat flow corresponding to the onset of thermal crosslinking and an exothermic chemical reaction. The dependence of the temperature of crosslinking with composition is shown in table 1. We believe that this is attributable to thermal crosslinking occurring via the carbon-carbon double bonds of the methacryloyl group.

Figure 1.

Table 1.

The time required for cross-linking to occur and the thermal stability of P(MMA/MAOEMA) were also investigated by solubility tests. Samples of polymer film were baked in a 90°C oven for 5 min, 30 min and 1 day.

After thermal treatment the solubility of the films in acetone was assessed as a means to gauge the degree of cross-linking. It was found that the lowest HEMA content films required more time to become crosslinked (i.e. become insoluble in acetone) than those having higher HEMA content. This trend probably relates to the onset temperature of the crosslinking as shown in the DSC data, so, for example, the 70% HEMA films became insoluble after just 5 minutes at 90°C, whereas the 34% HEMA film remained partially soluble after 30 minutes at the same temperature. To establish their overall stability all the polymers were found to remain stable when baked for 1 day at 120 °C. Melting point experiment revealed that all the polymers ultimately degraded at around 300°C

These results show that a polymer with more double bonds (i.e. more HEMA) crosslinks more easily at lower temperature, and that with longer heating all the polymers become crosslinked. These measurements provide important information about the thermal crosslinking parameters essential for waveguide fabrication. Partial thermal crosslinking offers additional potential for the fabrication of waveguides since after partial thermally crosslinking the process can be completed using UV thus allows a greater change in refractive index in the UV written waveguides.

Crosslinking Evidence

In order to gain better insight into the crosslinking behaviour of the polymers reported here during waveguide fabrication a number of spectroscopic studies have been carried out. In a typical procedure the polymer for the core layer is subjected to initial thermal crosslinking, followed by UV writing and finally further heat treatment when the cladding is processed. In a later section we report the results of refractive index changes observed in both raw and thermally crosslinked P(MMA/MAOEMA) as a result of UV exposure. It is thus clear that crosslinking is the critical process in forming these waveguides. Two techniques, IR (infrared) and solid state CPMAS NMR (nuclear magnetic resonance) spectroscopy were used fin an attempt to gain further insight into the chemical changes involved.

Initially, raw P(MMA/MAOEMA) was exposed under a low pressure mercury UV lamp (UVP pen-ray lamp). The reduction in intensity of the carbon-carbon double bond absorption at 1637 cm^{-1} in the IR spectrum (Figure 2) during this process provides clear evidence that the alkene side chains have been removed during photo-induced crosslinking of the polymer.

Figure 2

Similar results were obtained during thermal crosslinking of raw P(MMA/MAOEMA). Further support for the loss of alkene side groups came from solid state NMR spectroscopy (Figure 3). Polymer powder (~2g) was heated at 140°C for 2h and a sample (~0.5g) was retained for NMR measurement. After this thermal processing the double bond carbon resonances at δ 136.2ppm ($-\underline{C}=CH_2$), 126.4ppm ($-C=\underline{C}H_2$) and the ester carbon at δ 167.0ppm ($-O\underline{C}(=O)-$) of the HEMA sub-unit were found to have disappeared and chemical shifts for other carbons had shifted suggesting changes in the environment structure arising from thermal crosslinking (Figure 3 a and b). Thus thermally treated sample was then exposed under the UV lamp for 6h. During this time the sample was stirred frequently (every 30min) in order to give uniform exposure. Some evidence for structural modification during this process was obtained from solid state NMR spectra of the UV-processed polymers, slight changes being observed in the envelope at δ 62.6ppm (assigned to the methylene carbon of the HEMA sub-unit($-O\underline{C}H_2CH_2O-$)) (Figure 3c). This observation implies that, in even the absence of unsaturated cross-linking sites, the polymer structure is further modified upon uv-irradiation, whereas only the methacryloyl group is affected by thermal crosslinking. In addition, the chemical shifts of the main chain carbon atoms (δ 52.2 and 45.0 ppm) are not changed which means that the polymer is not degraded. After UV exposure the polymer was heated again to 140°C; no further changes were not detected in the spectra by this final heat-treatment.

In conclusion the evidence presented shows distinct signatures for both thermal and UV crosslinking. The UV crosslinking in P(MMA/MAOEMA) can occur via additional side chain processes allowing us to achieve additional crosslinking in already thermally treated layers. This UV-induced process provides the mechanism that allows us to write UV induced refractive index waveguides in this material.

It is well known that conventional PMMA is used for laser ablation[18,19]. It has been reported that the ablation process occurs through dissociation of the main carbon chain in PMMA resulting in degradation of a monomer under intense UV laser exposure. However, our polymer does not degrade under optimized exposure conditions. We think this is because our polymer is also thermally crosslinked and the additional linkages between polymer chains prevent degradation. Further studies at a range of wavelengths will be needed to prove this result.

Figure 3.

Photosensitivity of raw P(MMA/MAOEMA)

The UV direct writing process requires that the polymer should have good photosensitivity. In our initial channel waveguides the polymer for the core layer is thermally crosslinked. However, for some devices it is attractive to be able to use raw P(MMA/MAOEMA) as a core layer since it can have a greater photosensitivity and therefore we chose to investigate the photosensitivity of raw P(MMA/MAOEMA).

For the UV laser exposure, 6 mm spot size unfocused beams of four different powers (0.042, 0.077, 0.099 and 0.120 W corresponding to power densities of 0.0015, 0.0027, 0.0035, 0.0042 W/mm^2) were used. For each power the sample was exposed at six different fluences (0.102, 0.210, 0.310, 0.410, 0.510 and 0.760 J/mm^2) by controlling the exposure time. The refractive index (RI) was measured with a spectral ellipsometer. The RI increased linearly with increasing fluence, from 1.503 to 1.548 as shown in Fig. 5. Simultaneously the thickness decreased linearly from 15500 to 12500 Å (Figure 5). For a given fluence, the RI and thickness showed little systematic change with UV power density (Figure 6). The RI and thickness difference as a function of power density for the same fluence were close to the precision limit (within a range of ±0.003) of the instrument. We conclude that 47% HEMA content P(MMA/MAOEMA) is usefully photosensitive and that the refractive index and thickness changes depend primarily on total energy and not on power density. However, as we shall show later that power density becomes an important parameter when focus spots are used because of the very high power density obtainable.

Figure 4

Figure 5

Figure 6

Photosensitivity of thermally crosslinked P(MMA/MAOEMA)

In an actual waveguide the thermally crosslinked P(MMA/MAOEMA) serves as a core layer. Consequently the photosensitivity of thermally crosslinked P(MMA/MAOEMA) was studied by measuring the refractive index after UV exposure.

The ellipsometry system used in the previous section works well for determining RI and thickness of polymer films that are thinner than about 1.0 μm. However, for thicker films, such as actual waveguide layers, the accuracy of RI measurement by ellipsometry is poor. Thus the prism-coupling technique was adopted for measurements of layers served microns. The error range with prism coupling was within ± 0.001.

In order to use the prism coupling technique the film needs to be very uniform, which can be achieved by the use of a scanning of UV laser. The film was scanned with a 3 mm spot size unfocused beam of 0.140 W corresponding to power density of 0.02 W/mm^2. The separation between scans was 0.25mm and area for scan was 11x11mm^2.

The refractive index of the thermally crosslinked film was 1.498. After UV laser exposure at a fluence of 1.9J/mm^2 the RI increased upto 1.512 and thickness decreased from 4.36 to 3.31μm. The refractive index increase of the thermally crosslinked polymer upon UV exposure was found to be propotional to fluence (Figure 7). This data was taken with fluences of up to 1.9 J/mm^2. This is higher than the damage thresholds observed in later schannel writing experiments. In the channel experiments the power density was approximately one hundred time greater and so the result is not unexpected.

In conclusion the UV induced photosensitivity of thermally crosslinked P(MMA/MAOEMA) is sufficient to fabricate good quality channel waveguides. The Δn is higher than that achieved in UV written Ge-SiO$_2$ waveguides and therefore likely to be sufficient for making all UV written waveguides.

Figure 7

Waveguide fabrication

Silica with a refractive index of 1.457 served as the undercladding layer. The core layer was thermally crosslinked P(MMA/MAOEMA) and the channel was created by UV writing with the 244nm laser. The overcladding was again the same P(MMA/MAOEMA) which was thermally crosslinked after deposition.

The thickness change and shape of the UV-written waveguide was investigated using an α-step (before depositing the protective layer) (Table 2). The laser power was 1.0 mW (corresponding to power density of 12.73 W/mm^2). The calculation of fluence is based on an effective spot size of diameter 10 μm and area of $\pi(10/2\ \mu m)^2$. Six channels were made with different scan speeds. For exposure fluences of more than 0.637 J/mm^2, the polymer seemed to decompose. For exposure fluences of less than 0.318 J/mm^2 most of channels guided light. Using the cut-back technique the propagation loss through the channel waveguides (channel 3-6) was calculated to be less than 1 dB/cm with a coupling loss of around 4 - 7 dB.

Table 2

Investigation of waveguide profile on thermally crosslinked P(MMA/MAOEMA)

From the solid-state NMR results we have suggested that the thermally crosslinked P(MMA/MAOEMA) experiences further crosslinking under UV exposure. However the results from the channel waveguide fabrication experiments (Table 2) show that decomposition of the polymer occurs for higher fluences (>0.637 J/mm^2). Therefore we carried out studies to determine the maximum permissible fluences and power densities to avoid polymer degradation.

Laser beams of four different powers (0.0001, 0.0004, 0.0007, and 0.001 W corresponding to power densities of 1.27, 5.09, 8.91, 12.73 W/mm^2) were used. The spot size was 10 μm diameter. At all powers, the channels were written at seven different fluences (0.032, 0.064, 0.080, 0.159, 0.212, 0.318, 0.637 J/mm^2) by altering the translation speed of the layer under the laser spot. A SEM (scanning electron microscope) was used to image the profile of each waveguide (Figure 8).

Several clear trends are apparent from the samples. In particular we find that, at high power density and high fluence (e.g. figure 8a taken at 8.91W/mm^2 and a fluence of 0.637 J/mm^2), clear evidence is seen of damage to the waveguide involving material removal forming a curved channel with edges protruding from the surface indicating that the polymer flowed when the waveguide was written. At high power density and moderate fluence (e.g. figure 8b taken at 8.91 W/mm^2 and a fluence of 0.159 J/mm^2) we see narrow channels and little evidence of melting. This is because the faster translation speed results in less heating of the sample. At lower powers and lower fluences (e.g. figure 8c taken at 5.09 W/mm^2 and a fluence of 0.159 J/mm^2) no waveguide structure is visible in the SEM image however a good quality optical waveguide was observed by end-fibre launching. Even at the lowest power density we still observe damage at high fluence (e.g. figure 8d taken at 1.27W/mm^2 and a fluence of 0.637 J/mm^2).

In conclusion, we find that over the power density range used in the channel writing experiments (corresponding to realistic device writing times) the damage caused by the laser is largely dependent on the fluence, and does not depend strongly on the power density. As shown before, the achievable index change depends mostly on the fluence. Thus at reasonable power densities it is necessary to limit the fluence to limit damage. Fortunately, sufficient index difference may be obtained to write good quality low-loss channel waveguides at fluences as low as 0.032 J/mm^2. In a commercial process it would, of course, be possible to use a single laser for a large number of writing stages, or to use optics to deliver a number of spots on the same stage to write multiple devices thus increasing device output.

It is clear from the images and the laser power densities that localized heating can also contribute to the positive Δn change in the waveguides.

Figure 8.

Evaluation and discussion of waveguide and future work

In this report we have discussed a new polymer system suitable for direct UV writing of waveguides. The material has been thoroughly characterised to determine its thermal, and photosensivity properties. Research has been carried out into the underlying crosslinking mechanisms that make the system suitable for UV writing.

In future a number of improvements can be made to improve the performance of the waveguides. There are many ways to reduce the loss and increase the photosensitivity, in particular the photosensitivity of different HEMA content P(MMA/MAOEMA) copolymers will be investigated for the core and cladding layers in order to give higher phosensitivity. The undercladding can be changed from silica to a polymer to give better modal properties. We will also explore copolymers formed from fluorinated monomers for reduced IR loss. In addition different fabrication methods will be investigated. For example, the use of raw P(MMA/MAOEMA) for UV writing as the core layer instead of thermally crosslinked PMMA/MAOEMA) is expected to increase the achievable index difference.

In our experiments the optical loss was measured at 633nm for simplicity. Our focus in this work has been on researching the photosensitivity, mechanisms and techniques for direct UV writing in polymers, and so we have not concentrated on reducing losses. With suitable fluorination or deuteration this polymer system may be a suitable candidate for systems operating at 1.3 and 1.55μm. And, although, today, 1.3 and 1.55 μm are the preferred wavelengths for telecommunications, it may well be that in the future low-loss shorter wavelengths (e.g., around 800 nm) become particularly interesting for low cost local area networks.

Conclusions

Copolymers of MMA and HEMA have been prepared with a variety of HEMA compositions and have been successfully esterified using MAAN. Resulting novel functionalized polymers undergo crosslinking upon either heating or UV-exposure. Thermal crosslinking of polymers was confirmed by the disappearance of double bond absorptions in the infrared and solid state NMR spectra; 47 % HEMA content P(MMA/MAOEMA) crosslinks at 140°C, higher HEMA content (more double bonds) polymers crosslinking at lower temperatures. Once crosslinked, these polymers are stable up to 300°C. Further UV induced crosslinking of thermally crosslinked P(MMA/MAOEMA) is observed in the polymers and is useful for making channel waveguides. The photosensitivity of thermally crosslinked P(MMA/MAOEMA) was low, however this value of RI change is enough to guide light. Under the extreme exposure conditions achievable with focused lasers thermally crosslinked P(MMA/MAOEMA) degrade.

Under UV laser exposure, the RI of raw P(MMA/MAOEMA) increases linearly with an increase in the exposure fluence and the thickness decreases. The RI and thickness changes depend mostly on total energy but not on intensity of the imaging radiation.

Channel waveguides have been written with 47% HEMA-content thermally crosslinked P(MMA/MAOEMA). The propagation loss through the channel waveguide is calculated to be less than 1 dB/cm with a coupling loss of 4-7 dB. Future work is expected to lead to lower propagation loss and larger photosensitivity.

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