

# Solution doping of microstructured polymer optical fibres

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**Abstract:** Solution doping of microstructured polymer optical fibres [mPOF] is demonstrated, a technique which allows dopants to be introduced after polymerisation through the microstructure. Controlled diffusion is used to disperse the dopant uniformly across the fibre core, and the final concentration can be systematically varied by appropriate choice of conditions. We use this technique to produce a fibre doped with Rhodamine 6G and characterize its loss and fluorescence behavior.

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## 1. Introduction

The use of polymers to make microstructured optical fibres has made a variety of microstructures possible that cannot be easily made by the capillary stacking technique used for silica fibres. However the fabrication techniques generally used to produce mPOFs [1] have themselves made it problematic to produce doped fibres, because of their use of a monolithic preform. This suggests that the whole preform might need to be doped in order to

produce a doped fibre. In this paper we demonstrate that we are able to introduce dopants *through the microstructure* after polymerisation, rather than at the monomer stage as has been done in the past.

The result allows doped mPOFs to be made easily, using commercially available low-loss polymer. In doing so, this technique opens up a wide range of new applications of mPOF. These include applications that have been previously explored with conventional polymer fibres, such as fibre lasers [2,3] and non-linear optically active fibres [4], where the additional optical control available via the microstructure may be advantageous. We have also begun exploring the technique as a means of producing doped poled fibre to exploit the electro-optic effect [5]. As shown previously [6], the polymer walls between the holes of the microstructure in mPOF can be made less than a half a micron thick. Such structures are sufficiently thin that they can be considered as dense membranes. The ability to dope such membranes opens up the possibility of new applications such as biological sensing, where efficient optical detection would provide an attractive non-contact approach. Another possible application of the technique is to use chiral materials to produce circularly birefringent fibres.

## 2. Solvent diffusion in glassy polymers

At temperatures above the glass transition temperature of polymer diffusion can be described by Fick's laws [7], since in this case the mobility of the polymer segments is much greater than that of the penetrant molecules. In the glassy state however, deviations from Fickian behaviour occur because of the finite time required for the polymer molecules to accommodate the penetrant molecules. When the penetrant molecule mobility is much larger than the segmental relaxation the diffusion is known as "Case II diffusion". This is characterized by a sharply defined boundary between the swollen outer layer and the glassy interior of the polymer, and a diffusion front that advances with uniform velocity. The dopant plasticises the polymer and the penetration is proportional to the concentration at the front.

The transport of methanol in PMMA has been widely studied [eg. 8,9], including methanol/Rhodamine mixtures [10]. These studies show that at ambient temperatures it exhibits Case II diffusion, a result consistent with our results [see Fig. 1]. In our case the dye lags the solvent significantly, due to its larger size. Smaller molecules, such as iodine, apparently travel with the solvent [8]. The presence of dye molecules does not however seem to affect the passage of the solvent through the polymer [8,10]. It has been suggested [9] that the mechanical deformation of the polymer through the osmotic swelling due to the solvent is the most important driver of Case II diffusion. The dopant is able to diffuse relatively quickly through the polymer behind the solvent front.

Diffusion in PMMA is known to be influenced by a variety of factors including thermal history [9], specimen geometry [8], temperature [8,9] and solvent choice [10], amongst other factors. Thermal history, a factor that may be intimately related to how the sample has been processed, is known to be of particular importance.

## 3. Method and results

MPOFs are made using a two-stage draw technique [1]. Doping was carried out after the first draw, at the intermediate preform stage when the holes are about 250 microns in diameter-sufficiently large to allow solutions to pass through them. The preforms were annealed before doping to alleviate any residual stress, which could cause cracking when the solution was introduced, and also to ensure that prior thermal history did not play a role in determining the uptake of dopant.

The mPOF preforms were made using atactic polymethylmethacrylate (PMMA) supplied by VINK EXPORT, Belgium. Rhodamine 6G was obtained from Aldrich and used as supplied. It was dissolved in methanol, a good solvent for Rhodamine, but non-solvent for PMMA. Methanol is also quite volatile, having a boiling point of 60 °C, which allows it to be removed from the polymer below its glass transition temperature of 115 °C. A similarly appropriate choice of solvent would allow a wide variety of dopants to be introduced into PMMA.

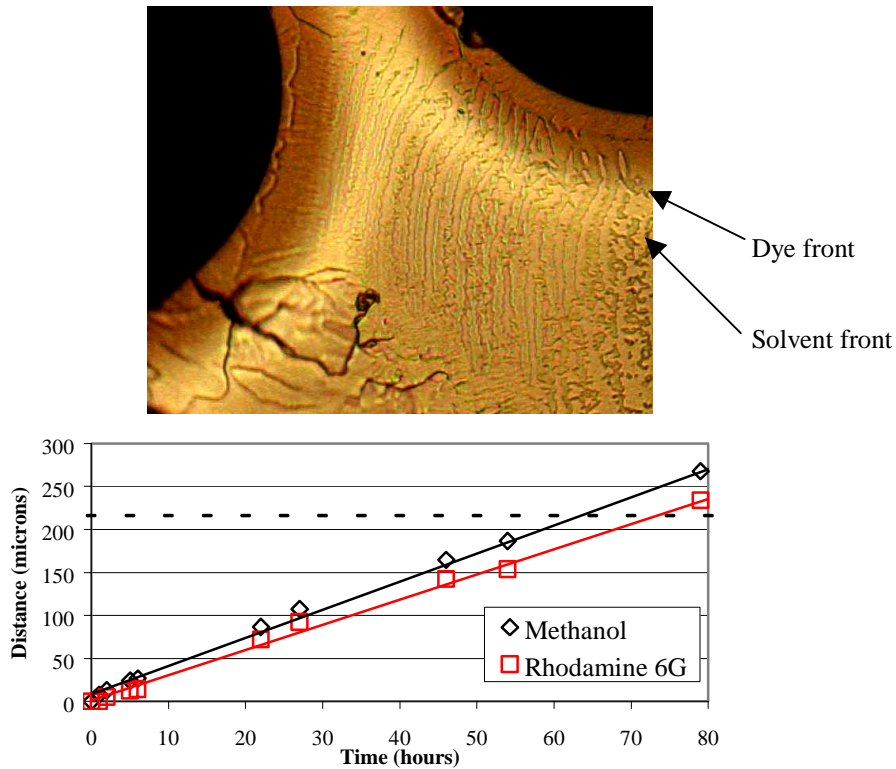


Fig. 1. Cross-section of preform during the doping, showing two holes adjacent to the core with the dye and solvent fronts diffusing in from the holes (top). Plot of the position of the dye and solvents fronts as a function of time (bottom). The linear dependence indicates Case II diffusion. The dotted line indicates the position of the core radius.

The preforms were left in a solution of the dye/methanol until the diffusion fronts had met at the centre of the core region, a process that took up to three days at room temperature, depending on the preform design. They were dried to remove the methanol from the PMMA, by heating at 90 °C for several hours and then drawn to fibre. The removal of the solvent from the polymer dramatically reduces the diffusion of the dye. After its removal there is no measurable change to dye distribution, even when the preform is maintained at elevated temperatures for extended periods [11].

The concentration of dye in the polymer can be varied by varying the dye concentration in the solution, the solvent system or the temperature. At higher temperatures the diffusion becomes increasingly Fickian, and the equilibrium dopant fraction increases. Using these techniques we have produced uniformly doped samples with dopant concentrations ranging from 1  $\mu\text{mol/L}$  to 1  $\text{mmol/L}$ . An example of a fibre doped using this method is shown in Fig. 2.

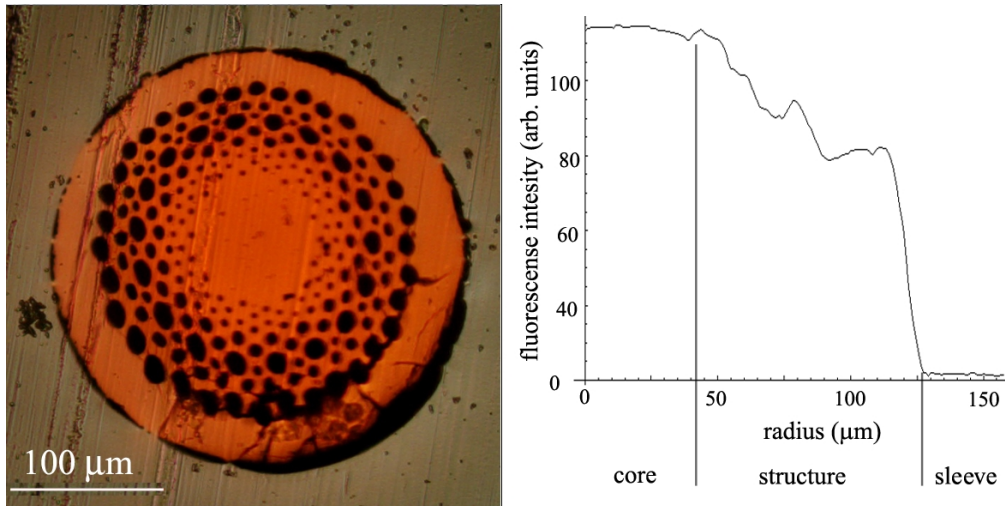


Fig. 2. Fluorescence intensity as a function of radius to show uniform doping in the core.

The preforms can also be removed from the solution prior to the dye fronts meeting in the core, at which stage a smaller amount of dopant has entered the polymer. Further diffusion during the drying stage results in a uniform dopant concentration, as shown in Fig. 3. The resulting dopant concentration is lower than if the solvent fronts had been allowed to meet. This offers an alternative route to controlling the concentration, in addition to control of the solution concentration and temperature.

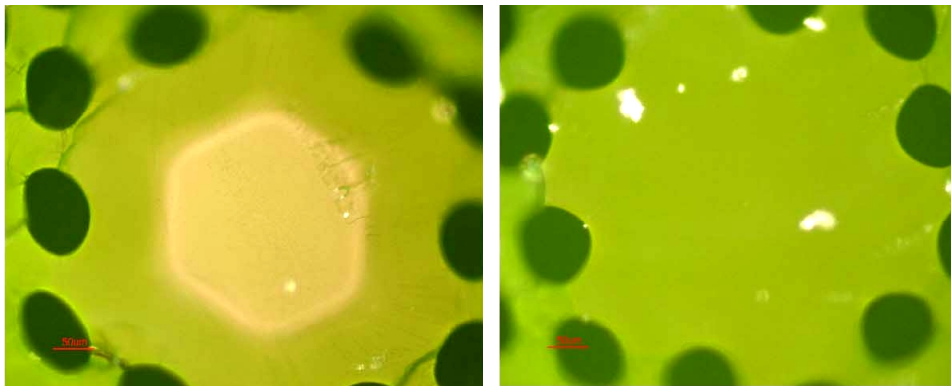


Fig. 3. Cross section of a preform removed from the solution prior to the solvent fronts meeting in the core (left) and the same preform after heating (right).

The complete removal of the solvent is clearly important. Thermo-gravimetric analysis [TGA] was carried out at the intermediate preform stage to determine whether solvent remained within the polymer matrix after the drying stage. The sample was heated at a rate of 2 °C/minute, and was then held isothermally at 250 °C for 10 minutes. There was no evidence of enhanced weight loss at or around the boiling point of methanol, indicating that it had been successfully removed. Rather there was a small continuous weight loss of 1.49%, over the course of the TGA run. This is probably due to a small amount of depolymerisation. Optical measurements [Fig. 4] also indicated that the process did not increase the attenuation of the

resulting fibre, other than through the expected absorptions due the dye. The absorption of the dye as well as the resulting fluorescence is presented in Fig. 5.

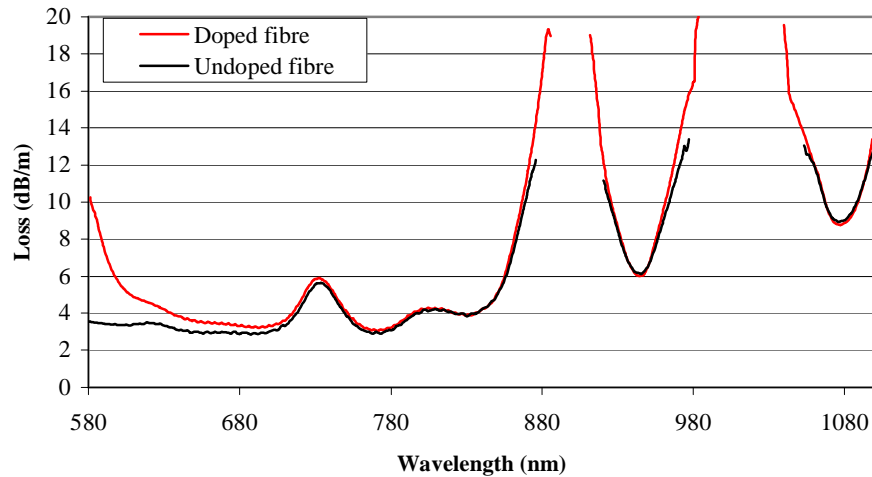


Fig. 4. Optical loss measurements of a doped and undoped fibre, drawn from the same preform, indicating that the doping does not introduce losses other than those due to the absorption of the dye (the sharp increase at the short wavelength region of the graph).

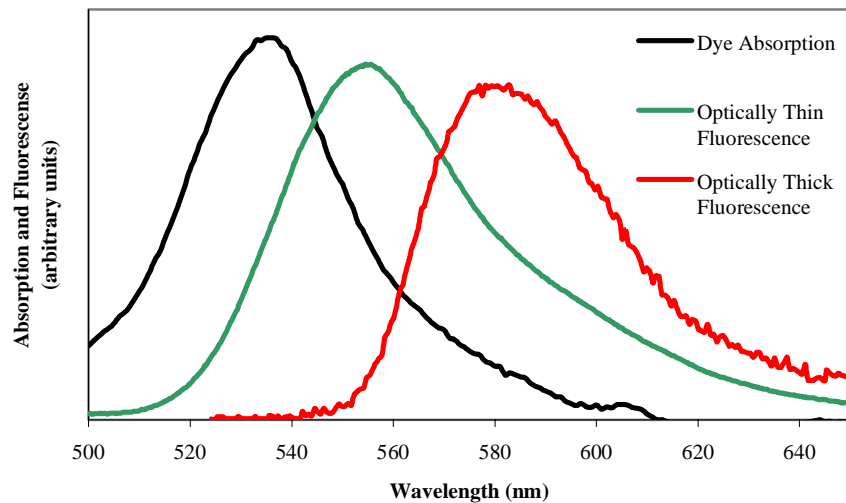


Fig. 5. The absorption spectrum of the Rhodamine 6G dye as determined by measuring the loss spectrum of a doped fibre and subtracting from it the loss spectrum of an undoped fibre. Two fluorescence spectra are also shown for a very short fibre (few millimetres) and a longer fibre (approximately 2 m). The shift to the red in the longer fibre results from re-absorption of the fluorescence by the dye. The fluorescence measurements were taken by launching light from an Argon-ion laser (514 nm – this laser line has been removed from the graph) into the core of the fibre. For a concentration around 1 mmol/L the absorption peak reached approximately 20 dB/m.

In an alternative technique, an acetone/Rhodamine solution was prepared and flushed through the preform, leaving a residual layer of dye, which subsequently migrated through the preform with heating. This process is faster but more difficult to control than the methanol method. As acetone is a solvent for PMMA, care must also be taken to avoid damage to the

microstructure. We note that different dye-solvent mixtures can result in very different concentrations in the final polymer, even when the concentrations in the starting solutions are similar.

Another approach that has been explored in the literature [10] is to expose the PMMA to the solvent prior to immersion in the dye-solvent solution. This greatly increases the speed of the dye uptake when it is exposed to the pre-swollen polymer. The dynamics of this system however are different to those of a “dry” sample immersed in a dye-solvent mix, and are characteristically Fickian in nature.

#### **4. Conclusions**

Our results show that it is possible to produce uniform doping in mPOF using commercially available dopants. These dopants can successfully be introduced after polymerisation, and are compatible with using a monolithic preform. Initial tests show that the solvent can be removed from the polymer matrix, and that the mobility of the dye without the solvent is so low that its subsequent diffusion is non-problematic.

We are beginning to exploit the possibilities presented by this new method. We have already explored it in the context of poling doped fibres [5] and were recently successful in producing the first mPOF dye laser [11]. In the future we hope to explore new applications, particularly in sensing, where the combination of a reactive surface or membrane, with efficient optical detection may prove valuable. We are also investigating the use of this methodology for the incorporation of inorganic dopants.

#### **Acknowledgments**

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