

# Doped Microstructured Polymer Optical Fibres

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**Abstract** *A method of doping is described, which allows dopants to be introduced after polymerization. The technique has been used to introduce Rhodamine 6G into the fibres, but is suitable for a large range of dopants.*

## Introduction

One of the advantages of using polymers for optical fibres is that it allows a wider range of dopants to be used. The lower processing temperatures used for polymers allow organics to be included- materials that would degrade at the much higher temperatures used for silica fibre drawing. This advantage however has traditionally been offset by the difficulty in simultaneously obtaining other optical properties, such as single modedness and low attenuation. Additionally, the introduction of dopants, particularly through incorporation into the polymer chain, can significantly affect the rheology, making drawing problematic.

In this paper we describe a new doping method which exploits the large surface area of microstructured polymer optical fibres (mPOF) to allow dopants to be introduced after polymerisation. In the examples we have studied, the technique does not affect either the drawing properties of the fibre, or cause additional attenuation. Its real significance however is that it enables the control of optical properties through the use of appropriate microstructures to be combined with the variety of material properties possible with polymers.

## Experimental Method

The doping technique relies on the diffusion of solvents in glassy polymers. The diffusion mechanism depends on a number of factors, most critically on temperature, which determines the relative mobility of the penetrant molecule and the polymer segments. At low temperatures the penetrant 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 by a diffusion front that advances with uniform velocity. The penetration of the solvent is proportional to the concentration at the front. A dopant dissolved in the solvent will also diffuse through the polymer either with, or behind the solvent front, depending on its

size. The solvent can subsequently be removed by heating.

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.

We have tested the methodology for dopants including Disperse Red (for the electro-optic effect) and Rhodamine 6G (for lasing applications). The dye was dissolved in methanol, a good solvent for the dye, but a non-solvent for PMMA. Methanol is also quite volatile, having a boiling point of 60°C, which allows it to be completely removed from the polymer below its glass transition temperature. The preforms were soaked in a dye/methanol solution until the diffusion fronts met at the core, a process that took up to 3 days, depending on the preform design. After drying, the preform was drawn to fibre in the usual way.

There are a number of variants on this basic method. For example we have explored the use of an acetone rather than methanol based solution. As acetone is a solvent for PMMA, it cannot be left in contact with the polymer for extended periods lest it damage the microstructure. It can however be flushed through the preform, leaving a residual layer of dye, which subsequently migrates through the preform with heating. This process is faster but more difficult to control than the methanol method. Another approach that has been explored in the literature [2] 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.

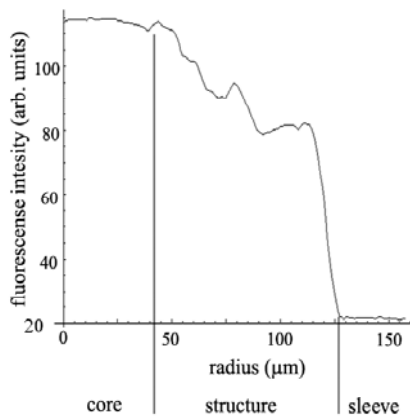
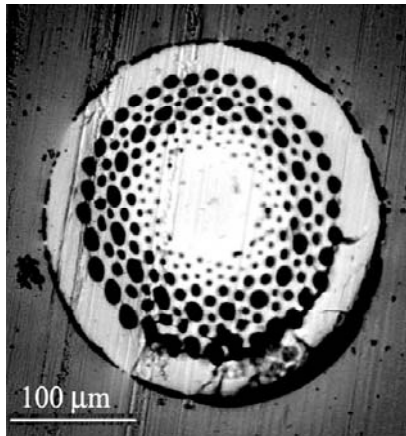


Figure 1: Fluorescence intensity as a function of radius to show uniform doping in the core.

The concentration in the doped region is uniform, as is expected for Case II diffusion. The concentration can be varied in a variety of ways. These include: varying the concentration in solution, the solvent used, the temperature, or the exposure time to the solution. If for example the perform is removed before the diffusion fronts meet, then subsequent heating will result in a uniform, but reduced, concentration in the core. Using these techniques we have produced uniformly doped fibre samples with dopant concentrations ranging from 1μmol/L to 1mmol/L. After the removal of the solvent, the dye does not diffuse noticeably, even when the sample is maintained

at 90°C for a period of 2 months.

An mPOF laser has been fabricated using these techniques [3] by doping PMMA with Rhodamine. As an amplifier, a gain in excess of 30dB was achieved.

### 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 perform.

We have shown previously that 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.

It may also be possible to use the technique to introduce inorganics into the polymer. Rare earth metal ions for example are used widely in inorganic and organic lighting medium as lighting centres. Jiacheng et al. [4] have shown through the study of nanocomposition, that Pr<sup>+3</sup>-doped polymer glass has the properties required to fluoresce, giving a handle on the synthesis of organic and inorganic nanocomposite optical fibre. The primary mode of introducing rare earth ions into polymers is to complex with organics. Such complexes could be diffused in a similar method to that described for dyes.

### References

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