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Obtainment of Graded Index Preforms by Combined Frontal Co-Polymerization of MMA and BzMA

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Summary. A simple system to obtain preforms with graded refraction index (GI) is presented. Index profiles with cylindrical symmetry are developed by introduction of a uniform rod of Poly Methylmethacrylate (65%)-co-Benzilmethacrylate (35%) (Poly-(MMA-*co*-BzMA)) during mass copolymerization of an 80% MMA – 20% BzMA solution of the same monomers. The obtained preforms present a gradual variation of the refraction index with approximate radial symmetry. Dripping of the central bar produces moderate variations of the index profile along the preform axis, but a large enough fraction of the obtained preforms have potential to produce graded index (GI) polymer optical fibers (POF) by subsequent drawing and to obtain flat polymeric lenses by slicing.

Keywords: BzMA; graded index perform; (GRIN preform); PMMA

Introduction

Diffusion of small molecules into a polymeric medium, whether they are involved in any chemical reaction or not, has long been used for the fabrication of a structural functional polymeric materials with a spatially varying properties along a specific direction.[1] Among them, gradient-index (GRIN) waveguides preforms have been obtained by molecular diffusion of non-polymerizable, small molecular weight, dopants introduced during the radical polymerization reaction of vinyl monomers.[1,2] This method takes advantage of the selective diffusion of high refractive index dopants during the polymerization gel phase and has shown to be useful for the production of POF's with high data transmission capability.[3–6] Inconveniently, however, the fixation mechanisms of the dopants involved in this method lead to low material long term stability under general operating conditions of the obtained fibers.[7] Other methods to obtain graded index preforms include the centrifugal driven diffusion of dopants during polymerisation,[8] the differential sedimentation of molecular components driven by ultracentrifugation of a copolymerizing mixture,[9] multiple feeding systems,[10] which require complex mechanical systems, and the annealing of co-extruded structures including migrating molecular species,[11] which again produce unreliable and long term unstable materials.

In this work we report a simple system to obtain a GI preform based on the swelling of a co-polymerized bar introduced in a mixture of the component monomers and the inter-diffusion of the involved molecular species, while polymerization of the unreacted mixture takes place, see Figure 1.

Experimental Part

Solutions of X_1 wt. % MMA and Y_1 wt. % BzMA, with 4.7×10^{-3} M of Lauroyl

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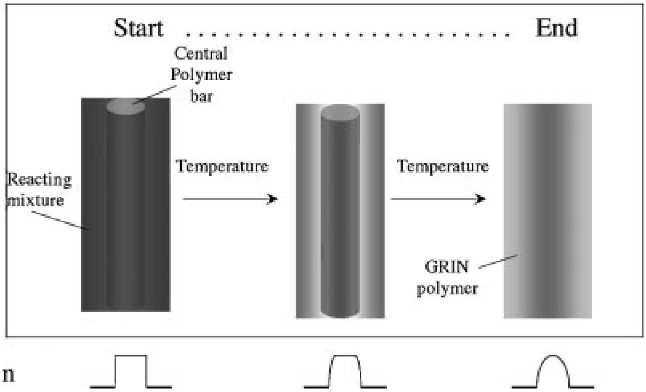

Figure 1.
Schematic representation of the preparation stages of graded index preforms. The expected time evolution of the refraction index in the radial direction is presented in the base line.

Peroxide as initiator and 2.36×10^{-2} M of n-Dodecyl Mercaptan as chain transfer agent were bulk co-polymerized by a frontal polymerization with gradual immersion (FPGI) method, within a borosilicate glass tube to obtain a cylindrical bar of 2 mm in diameter.[12] Figure 2 shows the refractive index and density as function of MMA concentration in the reacting solution. It is observed from it that BzMA acts as a nearly linear refractive index modifier agent, while density shows a more complex behavior but relatively smaller variations. The obtained bars were then centered with Teflon rings at the ends, within a second solution of X_2 wt. % MMA and Y_2 wt. % BzMA, with the same initiator and chain transfer agent concentrations in glass tube reactors of 20 mm inner diameter. The so prepared reactors were then introduced in a forced convection oven at 60 °C by 4 hours, after which the oven temperature was set to 120 °C by 3 hr, and finally cooled down to room temperature at a rate of about 2 °C/min. For each of X_1/Y_1 composition of the central bar, different X_2/Y_2 compositions

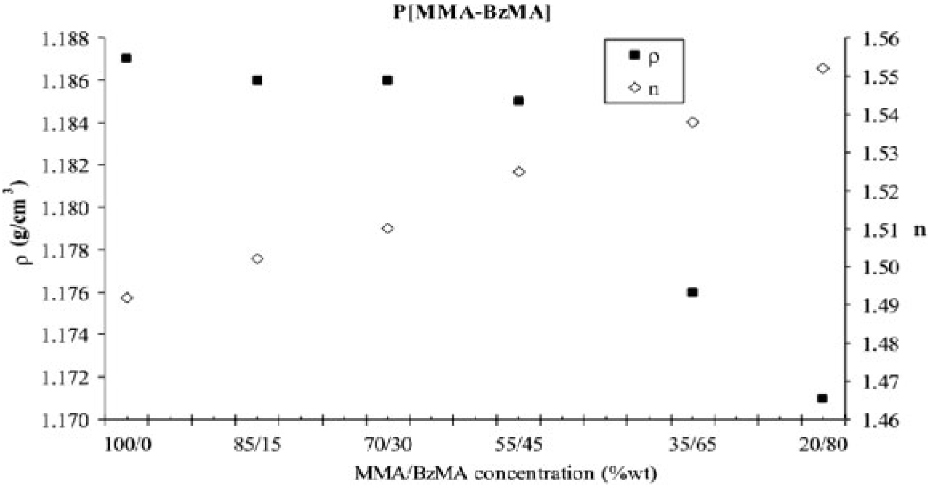

Figure 2.
Dependence of refractive index (n) and density (ρ) from MMA/BzMA concentration.

Table 1.
X/Y compositions tested in this study.

X/Y	65/35	70/30	75/25	80/20	90/10

were tried for the outer reacting solution. X/Y compositions were selected according to Table 1. In our experiments, most of the X_1/Y_1; X_2/Y_2 combinations produced bubbled materials. We concentrated in the 65/35; 80/20 combination since this system showed to be the one with the more uniform characteristics.

Results and Discussion

Slices of 5 mm of thickness were obtained from the best preforms to determine their refractive index profiles at different positions along the preform length. Figure 3 shows such profiles for a typical preform. A bending of the central bar is clearly observed, as noted by the profile center shift. However, such a bending, produces eccentricities lower than the 4% of the outer diameter in the upper half section of the preform and the radial symmetry have estimated deviations lower than the 1% of the same diameter. Dripping of the dissolved upper part of the central bar is also clear from the profile widening at the bottom of the preform.

By considering the obtained index profiles from the symmetry center to the inflection point of the corresponding curve, the profile shape parameter, α, defined by the best fit to the expression [13]

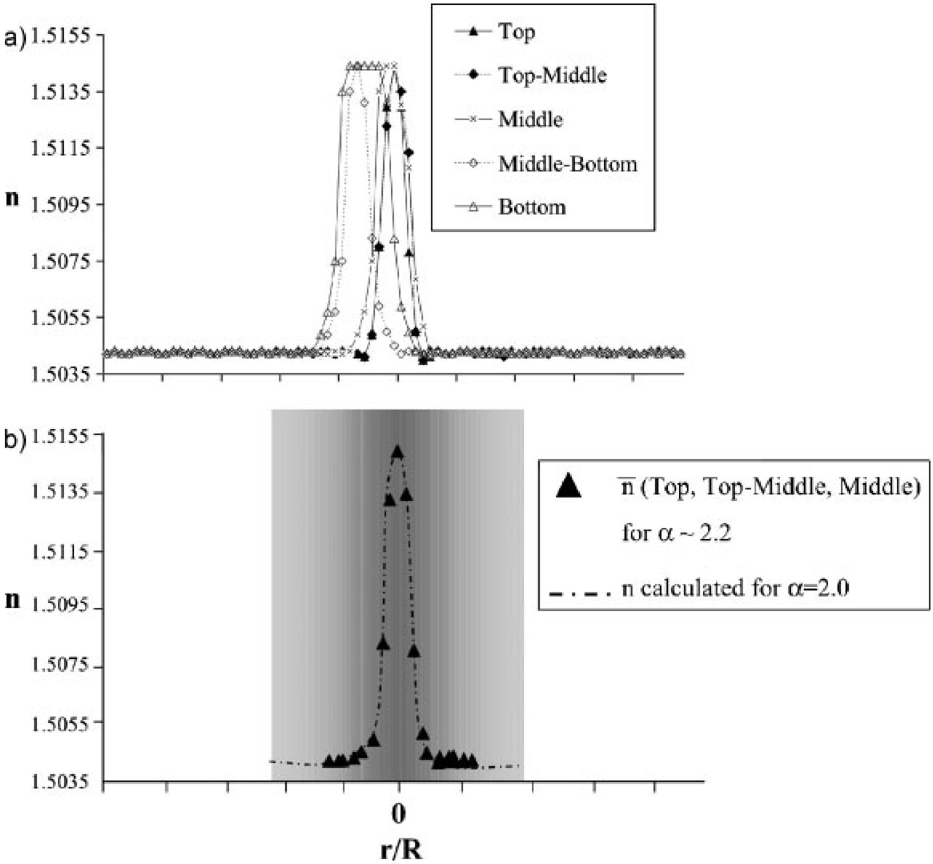

Figure 3.
Comparison between obtained GRIN profile (A) and adjusted profile for ideal α parameter (B).

$n(r) = n_0\sqrt{1-2\Delta\left(\frac{r}{R_0}\right)^{\alpha}}$, where n_0 is the refraction index at the center of the bar, was estimated to be between 2.1 and 2.2, which is promising for the obtainment of good GI-POF preforms. The corresponding index differences, given by $\Delta = \frac{n_0^2-n_1^2}{2n_0^2} \approx \frac{n_0-n_1}{n_0}$ for the highest transmission speed were between 0.0069 and 0.0071 (~0.01), so numerical apertures of about 0.19 could be expected in a fiber obtained by drawing the obtained performs.

Principle of Design

Independently of the practical difficulties faced in attaining uniform and non-bubbled materials, which should be addressed by optimizing reaction conditions (temperature, initiator, etc.), the techniques described above can in principle be used in a systematic way to design a polymer showing a refractive index with a better quasi-parabolic profile in the radial direction. A more precise design would require several concentric layers (e.g.: 4 to 6) of copolymer, each layer targeted for having a value of refractive index that corresponds to the ordinate of a point of a parabola at an abscissa value equal to the mean radius of the layer. The value of the refractive index calculated in this way would determine the necessary copolymer composition of each layer. It is known that the refractive index depends in a nearly linear way on the copolymer composition, as shown in Figure 2. For the system MMA/BzMA this linear relationship can be fitted to the equation:

$$n = 1.5643 - 0.0766 * F_{MMA} \qquad (1)$$

with an $R^2 = 0.997$, where F_{MMA} is the weight fraction of MMA in the copolymer and n is the refractive index of the copolymer. The limited interdiffusion of material of adjacent layers would smooth out the refractive index profiles approaching the parabolic shape.

An additional concern is how homogeneous the copolymer composition can be inside a given layer, without considering the contribution to heterogeneity due to interdiffusion, but just taking into account the inherent copolymer composition drift due to the different copolymerization reactivity ratios of the monomers. This is an important factor to evaluate as it sets a hard constraint for homogeneity given by the chemical nature of the monomers. This can be assessed by resorting to the predictions of the ultimate model for copolymerization. The copolymer composition (cumulative and instantaneous), assuming the terminal model, can be calculated in terms of conversion by using the following equations: [14]

$$\frac{dM_1}{dX} = -\frac{M_{1,0}+M_{2,0}}{1+\frac{M_2}{M_1}\left(\frac{M_1+r_2M_2}{M_2+r_1M_1}\right)} \qquad (2)$$

$$\frac{dM_2}{dX} = -\frac{M_{1,0}+M_{2,0}}{1+\frac{M_1}{M_2}\left(\frac{M_2+r_1M_1}{M_1+r_2M_2}\right)} \qquad (3)$$

$$F_1 = \frac{(M_{1,0}-M_1)*PM_1}{(M_{1,0}-M_1)*PM_1+(M_{2,0}-M_2)*PM_2} \qquad (4)$$

$$F_{1\_inst} = \frac{\frac{dM_1}{dX}*PM_1}{\frac{dM_1}{dX}*PM_1+\frac{dM_2}{dX}*PM_2} \qquad (5)$$

where M_1 and M_2 are the moles of unreacted comonomers (1 and 2 respectively) present when the total molar conversion is X; $M_{1,0}$ and $M_{2,0}$ represent the moles of each monomer charged to the reactor (at zero conversion), PM_1 and PM_2 are the molecular weights of the monomers, r_1 and r_2 stand for the copolymer reactivity ratios and F_1 and F_{1_inst} are, respectively, the cumulative and instantaneous copolymer weight fraction of monomer 1 at a given conversion. By integrating equations (2)–(3) and using equations (4)–(5) with $r_1 = 0.808$, $r_2 = 1.112$ (1 = MMA, 2 = BzMA),[15] the evolution of the cumulative and instantaneous weight fraction of the copolymer with conversion (wt. basis) was calculated and is shown in Figure 4 for two initial comonomer weight compositions (65/35 and 80/20). Due to the fact that the values of both copolymer reactivity ratios for this system are close to unity, the copolymer composition (microstructure)

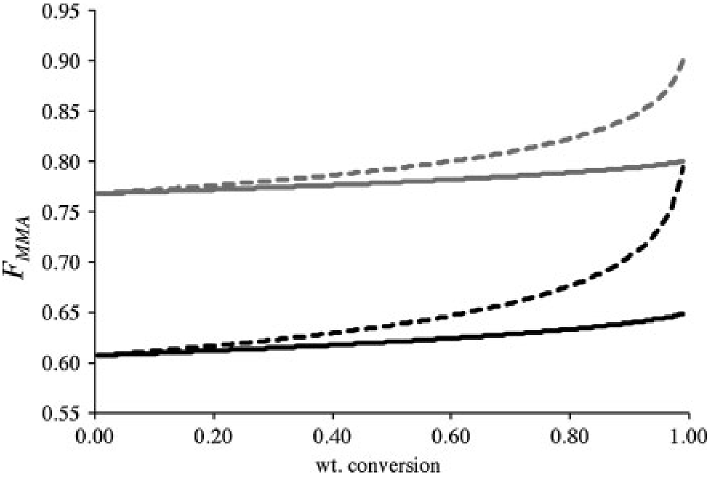

Figure 4.
Predicted variation of instantaneous (dotted line) and cumulative (solid line) weight fraction of MMA with conversion for the 65/35 (black lines) and 80/20 (red lines) MMA/BzMA copolymerization cases.

will tend to exhibit a random or Bernoullian behavior, although perfect randomness is only achieved for a hypothetical system in which both $r_i = 1$. This is hardly seen in practice, even for pairs of monomers with chemical affinity, so the randomness of the chain composition for the system MMA/BzMA is fairly reasonable, contributing to good optical properties. By looking at Figure 4, it is observed that the instantaneous composition of the copolymer produced during the reaction varies with conversion due to the composition drift in a range of approximately 0.13 and 0.19 (Δ wt. fraction) for the 80/20 and 65/35 case, respectively. Given the slope of eq (1), this represents a variation of refractive index of 0.0100 and 0.0145 respectively, for the maximum difference in the composition of instantaneous copolymer produced during the reaction in each layer. Although such a deviation at the end of the copolymerization reaction might be a factor to consider, for the radial polymerizing front of the studied system it would induce a reduction of the refractive index for the outer preform layers. The main effect of this would be a small reduction of the effective core diameter with an also small effect on the overall modal dispersion. The experimental results indicate that compositional variations at the end of the reaction do not have significant detrimental effects in the obtained performs.

Conclusions

We have presented a new method to obtain preforms with graded refraction index (GI), potentially useful to produce polymeric fibers with low modal dispersion, and correspondingly high transmission capability. The method is simple and takes advantage of the frontal copolymerization of MMA and an affine comonomer. As indicated, further refinements of this method can be achieved based on a simple copolymerization model.

The determined parameters for prototype performs obtained by the presented method are promising to produce GI-POF's.[16] Further studies are under way to avoid the central bar bending and to compensate for material dripping.

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