Fabrication of a Gradient Refractive Index Preform Using Laminar Shear Mixing

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ABSTRACT: A gradient refractive index rod was successfully prepared by a new fabrication method using laminar shear mixing, and a graded index polymer optical fiber that satisfied IEEE1394b was obtained from the method. To fabricate the gradient refractive index rod, a liquid monomer mixture with a relatively low refractive index was placed in a prepared cylindrical glass reactor and a transparent polymer rod with a higher refractive index was introduced at the center of the reactor. The reactor and the polymer rod were then rotated concurrently with a small rotating speed difference to generate a Couette flow in the liquid phase. The centrifugal force generated by rotation and the polymer diffusion into the liquid monomer mixture developed a graded concentration profile in a radial direction. The Couette flow could reduce the concentration fluctuation in a tangential direction. In addition, the graded index profile could be controlled by the copolymer composition of the rod and its diameter. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 95: 1100–1104, 2005

Key words: laminar shear mixing; gradient refractive index; polymer optical fibers; diffusion; centrifugal force

INTRODUCTION

Diffusion between two or more chemical species, whether they are involved in a chemical reaction or not, has long been used for the fabrication of specially structured functional material such as the production of an object that possesses a spatially varying property along a specific direction. Among them, a gradient refractive index (GRIN) rod is usually fabricated via molecular diffusion of nonpolymerizable species (dopants) coupled by a radical polymerization reaction of vinyl monomers. This method is well known as an interfacial gel polymerization technique that exploits the exclusive diffusion of bulky dopants with high refractive indices during the phase in which the gel is being polymerized.[1,2] The Koike group has reported that graded-index (GI) polymer optical fibers (POFs) based on a poly(methyl methacrylate) (PMMA)–dopants system has a high data transmission speed.[3–6] The group obtained the GI-POFs by thermally drawing the GRIN preform and using an avalanche photo diode and laser source to measure the transmission speed.[7]

GI-POFs based on PMMA have since attracted attention because of their low cost, high numerical aperture, and high flexibility. Accordingly, new fabrication methods for a GRIN rod have been studied intensively. The typical methods include a centrifugal diffusion polymerization method with dopants,[8] a dopant-free ultracentrifugal method,[9] and an extrusion method.[10]

In the ultracentrifugal method, GI profiles are generated by the balance between the centrifugal force and Brownian diffusion; the created GI profiles are then fixed via polymerization. Unfortunately, this method has a problem inevitably derived from volume shrinkage. Although monomer fills the rotating reactor, a preform with a central cavity around the rotation axis is made under the centrifugal force field due to volume shrinkage. Accordingly, when an optical fiber is fabricated using a preform in which the volume has shrunk, a discontinuous refractive portion appears proportional to the volume of the vacancy, which leads to a remarkable reduction of transmission.[11] The centrifugal diffusion polymerization method has the same drawback, too.

The extrusion method extracts material of low molecular weight and high refractive index from fiber; it also extracts material contrarily introduced in a radial

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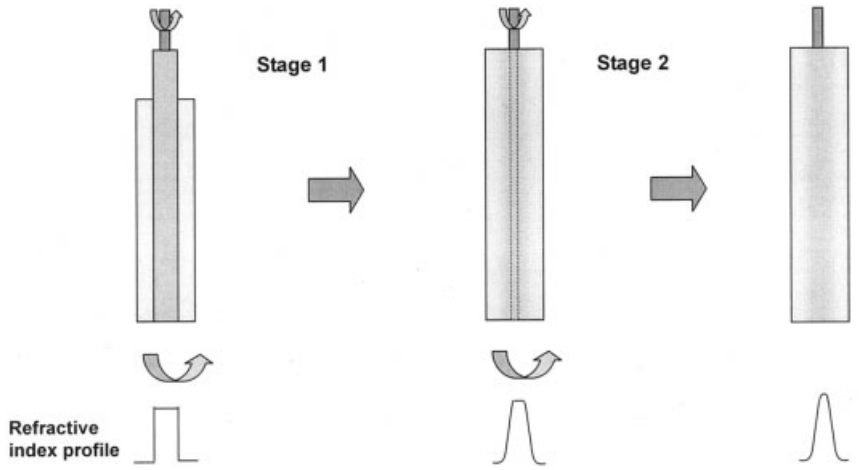

Figure 1 Schematic illustration of the LSM method.

direction to obtain GI-POF. However, this method has problems in reliability, production yield, and long-term stability because of the presence of easily migrating dopants.

In this paper, we report a new fabrication method, the laminar shear mixing(LSM) method. In the LSM method, GI profiles are developed by concurrently rotating a copolymer rod and a reactor. A copolymer rod placed at the rotating center has a higher refractive index and density than that of the surrounding monomer mixture. The copolymer rod and the reactor containing the monomer mixture rotate with a slight difference in the revolution speed to generate a Couette flow. The preform fabricated by the LSM method has several advantages; it has no central cavity or long-term stability because this method requires a low revolution speed and does not use any dopants.

EXPERIMENTAL

Materials

We purchased the following from Aldrich: methyl methacrylate (MMA), benzyl methacrylate (BzMA), α,α'-azo-bis(isobutyronitrile) (AIBN) as an initiator and *n*-butyl mercaptan as a chain transfer agent. We purified the monomers MMA and BzMA by distillation under reduced pressure after extracting inhibitors with an aqueous 0.5 *N* sodium hydroxide solution, washing with distilled water, and drying with sodium sulfate.

Copolymer rod synthesis

We prepared a poly(methyl methacrylate)-*co*-poly-(bezyl methacrylate) (PMMA-*co*-PBzMA) rod by bulk polymerization in sealed glass tubes under a nitrogen atmosphere using a Branson Ultrasonic Cleaner bath (Model No. 5510) at 60°C for 48 h. The MMA and BzMA mixture (80/20, mol %/mol %) was inserted into a glass tube with an inner diameter of 20 mm and a length of 150 mm. The mixture was degassed through several freeze–thaw cycles. We added 0.03 mol % of AIBN to the mixture as a thermal initiator and 0.3 wt.% of *n*-butyl mercaptan as a chain transfer agent.

We performed postpolymerization for 24 h at 80°C and then for 24 h at 110°C. Finally, we prepared the copolymer rods by breaking the glass tube with care.

Preparation of GI-POF preforms

A schema of the preform fabrication is shown in Figure 1. The preform was prepared in two stages: GI profile generation and fixation. In stage I, the copolymer rod, with a diameter of 20 mm, rotated at 25 rpm at room temperature for 5 h; the reactor containing the monomer mixture (MMA, 0.03 mol % AIBN and 0.3 wt.% *n*-butyl mercaptan) rotated concurrently at 20 rpm. In stage II, we raised the temperature of the reactor to 60°C and maintained this for 4 h to fix the generated GI profile via polymerization. Postpolymerization was performed for 24 h at 75°C and then for 24 h at 85°C under a vacuum. The preform was then drawn to a fiber with a diameter of 750 μm.

RESULTS AND DISCUSSION

Fabrication of a GI-POF preform

A GI-POF preform was fabricated in two steps. The copolymer rod (n = 1.5056, density = 1.19) was inserted into the tube reactor containing the monomer mixture (n = 1.414, density = 0.936) and placed at the center axis. The copolymer rod and the reactor were then rotated concurrently with a slight difference in revolution speed to generate a Couette flow. If the concentration profile along the radial direction is gen-

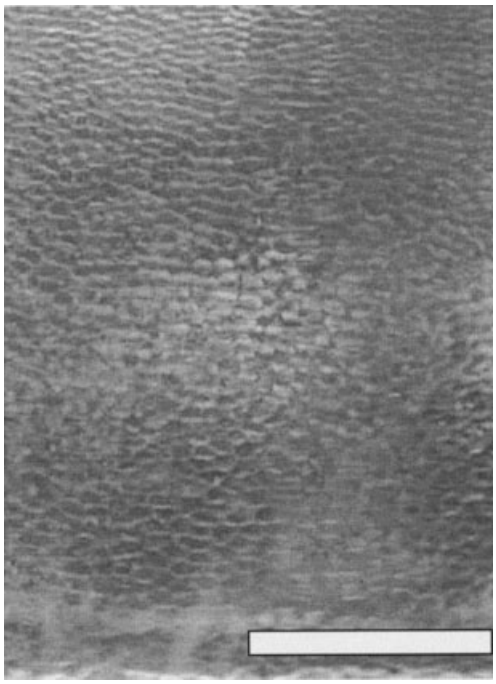

Figure 2 Photograph of the surface of a copolymer rod diffusing into the monomer region under no flow. The indented surface indicates that the concentration is also indented. Scale bar: 5 mm.

erated by diffusion only, without a Couette flow, the copolymer rod has an indented concentration profile in a tangential direction as shown in Figure 2. The concentration fluctuation along the tangential direction was not observed in the preform fabricated under the Couette flow. This phenomenon is important evidence that the Couette flow can reduce the concentration fluctuation in the tangential direction.

In the early stage, the concentration shows a step profile in the radial direction. As time elapses, the profile becomes smooth because the copolymer rod is dissolved into the monomer and the monomer consequently diffuses into the copolymer rod (stage I). In addition, the copolymer tends to move toward the monomer region by centrifugal force because the density of the copolymer is higher than that of the monomer. This phenomenon implies that the step concentration profile continuously changes to generate the GI profile and will eventually become flat after a long time. Therefore, to obtain the GI shape, the generated profile should be fixed at a certain time, which can be done by polymerization of the monomer since polymerization induces an increase in the viscosity of the medium; finally, the medium is glassified (stage II). The copolymer rod gradually thins until it eventually separates from the rotating axis. We introduced the polymerization before the copolymer rod separated from the axis. After finishing the polymerization, we successfully obtained a GI-POF preform.

Characteristics of the preform

The composition of the preform along the radial direction was measured by H^1-NMR as shown in Figure 3. The formula $\Delta C(r/R)$ is defined as

$$\Delta C(r/R) = C(r/R) - C(1), \tag{1}$$

where $C(1)$ is the concentration at the periphery, $C(r/R)$ is the concentration along the radial distance, r is the radial distance, and R is the radius of the preform.

This figure shows that $\Delta C(0)$ is 0.18 and the ΔC profile has a parabolic shape. In the early stage, $\Delta C(0)$ was 0.2 (the initial composition of the copolymer rod), and the final $\Delta C(0)$ was reduced to 0.18, showing that the monomer is well diffused into the copolymer rod. The optical properties of the preform are dependent on these parameters ($\Delta C(0)$ and ΔC shape) because $\Delta C(0)$ is directly related to the refractive index and the numerical aperture, and the ΔC profile shape is closely related to the data transmission speed. Since the concentration (copolymer composition) is linearly related to the refractive index of the copolymer,[11] the concentration profile can be converted into a refractive index profile. The $n(r/R)$ with r/R is shown in Figure 4. Generally, the GI profile of the preform (core part) can be written as[12]

$$n(r) = n_0 \sqrt{1 - 2\Delta\left(\frac{r}{R}\right)^g}. \tag{2}$$

Here r is the radial distance from the center of the preform, R is the radius of the preform, n_0 is the refractive index at the center of the preform, and n_1 is the refractive index at the periphery of the perform, and the dimensionless parameter g is defined as the

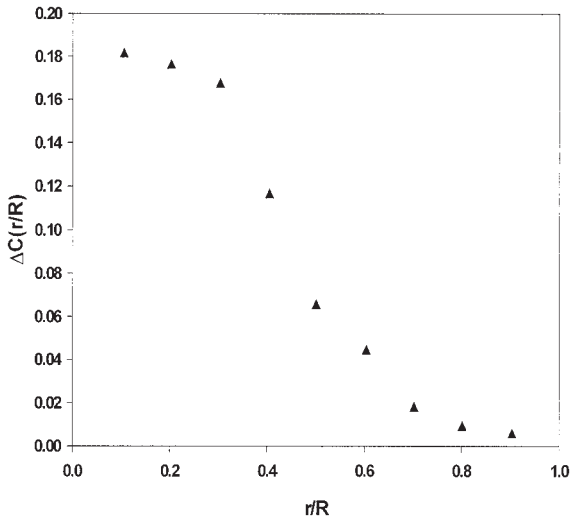

Figure 3 $\Delta C(r/R)$ profile with r/R.

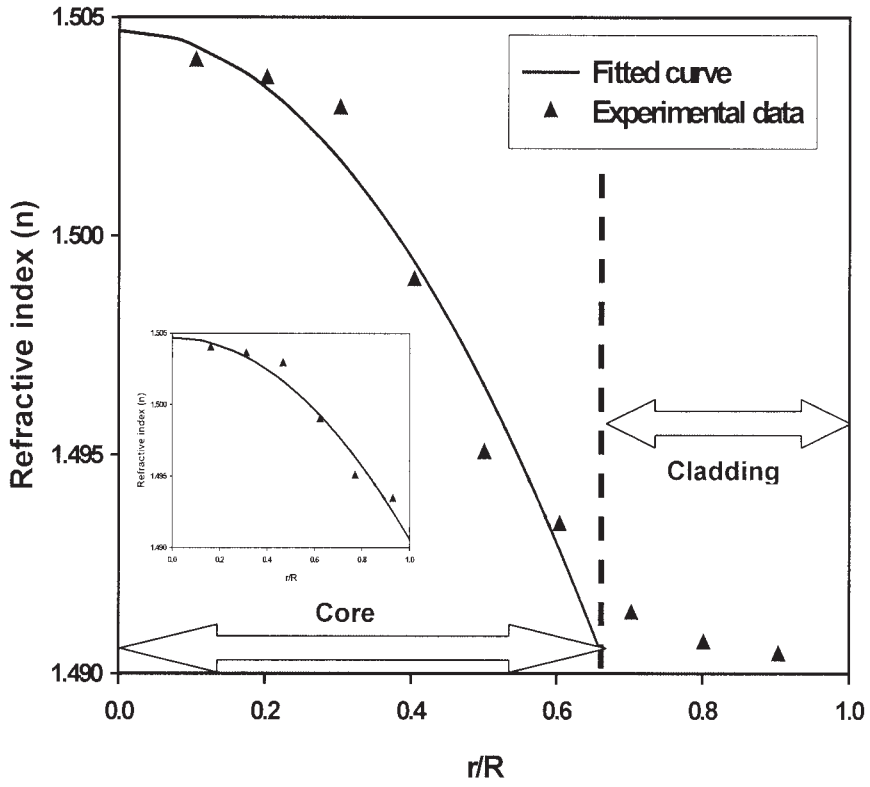

Figure 4 Refractive index profile with r/R. The triangular dots represents experimental data and the solid line represents fitted data by Eq. (2) with $n_o = 1.5047$, $\Delta = 0.0094$, $g = 2.01$. The inset shows a rescaled refractive index profile.

index profile shape. The index difference (Δ) is defined as

$$\Delta = \frac{n_0^2 - n_1^2}{2n_0^2} \approx \frac{n_0 - n_1}{n_0}. \quad (3)$$

The transmission speed is highest when g is about 2 and Δ is 0.01 to 0.02 if there is no material dispersion.[12–15] To evaluate Δ and g of the core part, we plotted $\log\{1 - [n(r)^2/n_0^2]\}$ with $\log(r/R)$ after we rescaled $r/R = 0.65$ (end of core part) to 1, as shown in the inset of Figure 4. In this graph, the slope corresponds to g and the extrapolated value at $\log(r/R) = 0$ corresponds to $\log 2\Delta$.[11,16] The evaluated g and Δ are 2.01 and 0.0094, respectively, (see GI-POF-4 in Table I).

TABLE I
The g and Δ Values of Preforms Prepared under Various Experimental Conditions

Preform	Rod composition (PBzMA mol %)	Rod diameter (mm)	Mixing time (h)	Δ	g
GI-POF-1	15	10	3	0.0062	3.12
GI-POF-2	15	20	5	0.0078	2.20
GI-POF-3	20	10	3	0.0070	2.96
GI-POF-4	20	20	5	0.0094	2.01

Replacing g and Δ with Eq. (2), the refractive index profile was plotted as shown in the inset of Figure 4. After rescaling $r/R = 1$ to 0.65, the refractive index profile is shown in Figure 4. The g and Δ values of the preforms prepared under various experimental conditions are listed in Table I. We compared the g and Δ values with the copolymer rod composition and its diameter. A lower PBzMA composition means a lower refractive index copolymer (PMMA-*co*-PBzMA) because PBzMA ($n = 1.568$) has a higher refractive index than PMMA ($n = 1.49$). Accordingly, the Δ values of the preforms with a lower PBzMA composition (GI-POF-1 and GI-POF-2) are smaller than that of higher cases (GI-POF-3 and GI-POF-4). A smaller rod diameter requires a shorter mixing time because the smaller rod separates from the rotating axis more quickly. The g values of the preforms with a smaller diameter have a larger value than that with a bigger diameter. The reason is schematically illustrated in Figure 5. Since the rod with the larger diameter has a wider diffusion region (copolymer rod region), it reveals a smoother profile. Hence, the profile shape becomes smooth, causing a smaller g value as the rod diameter increases.

The preforms were thermally drawn to the fibers with 750 μm diameter. Attenuation was measured using a cutback method and the bandwidth of each

fiber was measured using a pulse-broadening method. Each value is listed in Table II. Attenuation is affected by the inherent absorption of materials and external impurities.[17] All GI-POFs show that the external impurities are mostly eliminated because the inherent absorption of PMMA is approximately 180 dB/km at a 650-nm wavelength.[17] These attenuations are sufficiently low to use commercially. As expected, the g values GI-POF-2 and GI-POF-4 have a relatively large bandwidth because the g value is around 2. Bandwidth, which is a function of Δ and g values, becomes large as the Δ value decreases; however, the numerical aperture also diminishes as the Δ value decreases, and thus the adequate Δ value is about 0.01. Consequently, GI-POF-2 has a higher bandwidth than GI-POF-4. All g values are sufficiently large to satisfy IEEE1394b.

CONCLUSIONS

GI-POF preforms were successfully fabricated using the LSM method. The concentration fluctuation in the tangential direction was greatly reduced by a Couette flow. The Δ and g values could be controlled by the copolymer rod diameter and composition. Namely, the Δ value increased with the PBzMA composition and the profile shape (g value) became smooth as the copolymer rod diameter increased. The thermally drawn fibers that were 750 μm in diameter showed sufficiently low attenuation and high bandwidth to satisfy the IEEE1394b. The GI-POF preforms can be used as polymeric lenses, and the GI-POF drawn from it can be used for image guides and communication systems such as local area networks and home networks.

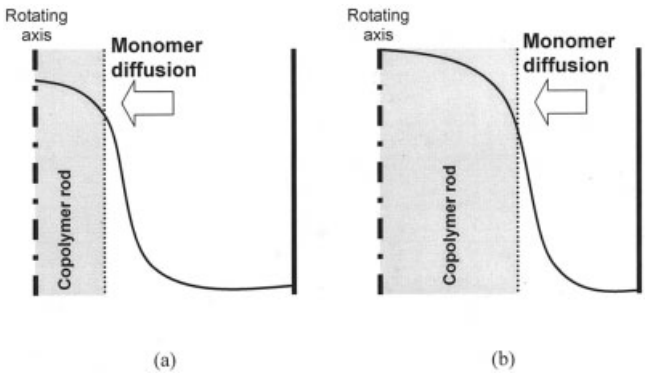

Figure 5 Schematic illustration on the formation of a refractive index profile shape. The rod diameters are (a) 10 and (b) 20 mm.

TABLE II
Attenuation and Bandwidth of Each Fiber

Fiber	Attenuation (dB/km)	Bandwidth (GHz at 100 m)
GI-POF-1	210	1.56
GI-POF-2	198	2.56
GI-POF-3	226	1.58
GI-POF-4	201	2.02

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