Combined Frontal Polymerization for Preparation of Refractive Graded-Index Polymer

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Abstract

In this work, a novel fabrication method, what-we-call, Combined Frontal Polymerization (CFP) is proposed and investigated. For a CFP method, GI (Graded Index) profiles are developed generating a controlled central rod of Poly MethylMethacrylate-co-BenzilMethacrylate (P[MMA-BzMA]) generated with a developed Modified Frontal Polymerization (MFP) technique and then immersing it into a co-monomer mixture. The final preform has a reduced radial fluctuation in concentration because of: initial uniformity of the composition of central rod and thermally migrating mixture of the external monomers. The preform fabricated by the CFP method has several advantages: it has long-term stability because this method requires molecular weight controlled central rod (± ~4%) gotten by MFP, does not use any dopant and can be used as polymeric lenses, and the Graded Index Polymer Optical Fiber drawn from it can be used for image guides and communication systems such as local area networks and home networks.

1. 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 material such as the polymeric 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 small molecular weight and non-polymerizable specie (dopant) coupled by a radical polymerization reaction of vinyl monomers. This method is well known interfacial gel polymerization technique which exploits the exclusive diffusion of bulky dopant with high refractive indices during the phase in which the gel is being polymerized [1,2]. Koike et al. has reported that graded-index (GI) polymer optical fibers (POFs) based on a polymethylmethacrylate (PMMA) and dopants system has a high data transmission capacity [3-6]. These GI-POFs based on PMMA have since attracted attention because of their cost-effectiveness, 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 [7], a dopant-free ultracentrifugal method [8], an extrusion method [9], and multiple feeding method [10].

In this work, a novel fabrication method, what-we-call, Combined Frontal Polymerization (CFP) is proposed and investigated. For a CFP method, GI (Graded Index) profiles are developed generating a controlled central rod of Poly MethylMethacrylate-co-BenzilMethacrylate (P[MMA-BzMA]) generated with a developed Modified Frontal Polymerization (MFP) technique and then immersing it into a co-monomer mixture. The final preform has a reduced radial fluctuation in concentration because of: initial uniformity of the composition of central rod and thermally migrating mixture of the external monomers. The preform fabricated by the CFP method has several advantages: it has long-term stability because this method requires molecular weight controlled central rod (± ~4%) gotten by MFP and does not use any dopant.

2. The concept of CFP

Principle of CFP

The concept of our new GI preform fabrication method is the diffusion of the polymer into the liquid monomer phase as shown in Figure 1. A cylindrical glass tube reactor was filled with the mixture of monomer (liquid phase), initiator and chain transfer agent with a lower refractive index and density, and then a copolymer and very homogeneous rod (solid phase) with a higher refractive index and density was placed in the center of reactor. As the concentration profile is obtained by only diffusion (without rod rotation), one can easily imagine that the tangential concentration profile is not homogeneous, but in our case, it is homogeneous because of the very controlled molecular weights of the central rod. On the other hand, the diffusion between interfaces due to homogeneous migration of species gives that, the concentration fluctuation of tangential direction can be greatly smooth without using different speed between the rod and the tube reactor, and it looks like generates homogeneous shear flow [11].

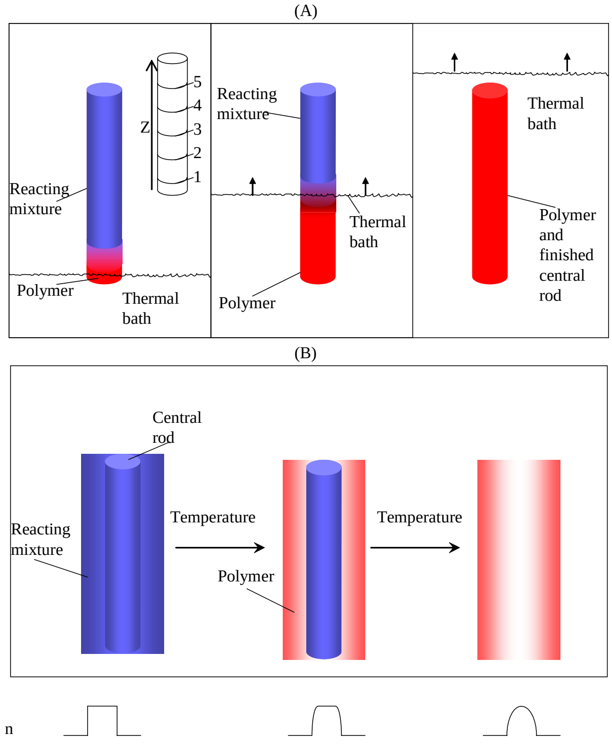

Figure 1. General scheme of CFP: (A) Generation of central rod.
(B) Introduction of central rod into reaction mixture to get a GI profile (n).

In Figure 1 (A), the central rod is generated with a minimum of molecular weight fluctuations and therefore in the polymer density.

In Figure 1 (B), the reactor and the rod are heated together for enough time to obtain smooth concentration profile, and then temperature is elevated in order to fix a generated profile (Figure 5).

Figure 2 shows the schematic of CFP process in cylindrical coordinate. The reaction tube of diameter R_0 and the copolymer rod of diameter κR_0 located in the center of reaction tube. The vacant space between reaction tube and copolymer cylinder is filled with comonomer reaction mixture of lower refractive index.

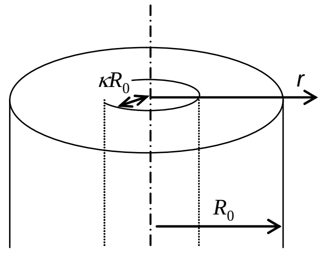

Figure 2. Cylindrical coordinates of coaxial arrange CFP process.
κ is the ratio of central rod's radius versus that of tube ($0 < \kappa < 1$).

2. Experimental conditions

Since the attenuation loss of POF is influenced by even small amount of impurities, purification of all monomers and additives are of crucial importance in manufacturing POF. In most cases, the external factors of the attenuation loss come from impurities which are not fully removed during purification process and bubbles or imperfections which are created during manufacturing. In the purification process of monomers and additives, all extrinsic factors such as metal, dimmer, gaseous components should be eliminated. All materials are purified at our best and the impurity level in monomers and additives are fully investigated prior to polymerization. Because of monomers were dried by a molecular sieve until water content, determined by the Carl Fisher method, was below 0.02%. Inhibitor was then removed at 60 ^{o}C and high vacuum distillation. Purity was evaluated, by Gas Chromatography (GC), to be better than 99.98% before polymerization procedures. DDM, from Aldrich, was also purified by vacuum distillation. Purity, also evaluated by GC, was better than 99.50%. 99.95% LP, from Akzo Nobel was used as received but active oxygen was determined to be 4% at least confirmed by iodimetry method. 99.99% Helium from Grupo Infra was used as a sweeping gas to remove dissolved gases in the prepared reacting mixtures. All of the reactions were carried out within borosilicate glass tubes washed with neutral soap followed by immersion of nitric acid (5%) with distilled water and rinsed with deionized water.

3. Results and discussion

Fabrication of GI-POF preform

A GI preform was fabricated in two steps. The copolymer rod Poly(MMA-co-BzMA) (65mol%/35mol%) (n = 1.5146, density = 1.185 g/cm^3) was inserted into the tube reactor containing the co-monomer mixture MMA/BzMA: 80mol%/20mol% (n = 1.417, density = 0.941 g/cm^3) and placed at the center axis. As the concentration profile along the radial direction is generated by diffusion only, without additional process only using a controlled molecular weight rod, the concentration fluctuation along the tangential direction was not observed in the preform fabricated. This phenomenon is important evidence that the using a special rod 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 (Fig. 1 (B)). In addition, the copolymer tends to move toward the monomer region by migration 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 (Fig. 1 (B)). The copolymer rod gradually thins until it eventually separates from the 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 perform

The composition of the preform along the radial direction was measured by ABBE refractometer as shown in Figure 3. The formula $\Delta n(r/R_0)$ is defined as:

$$\Delta n(r/R_0)=n(r/R_0)-n(1) \qquad (1)$$

where $n(1)$ is the refractive index at the periphery, $n(r/R_0)$is the refractive index along the radial distance, r is the radial distance and R is the radius of the preform.

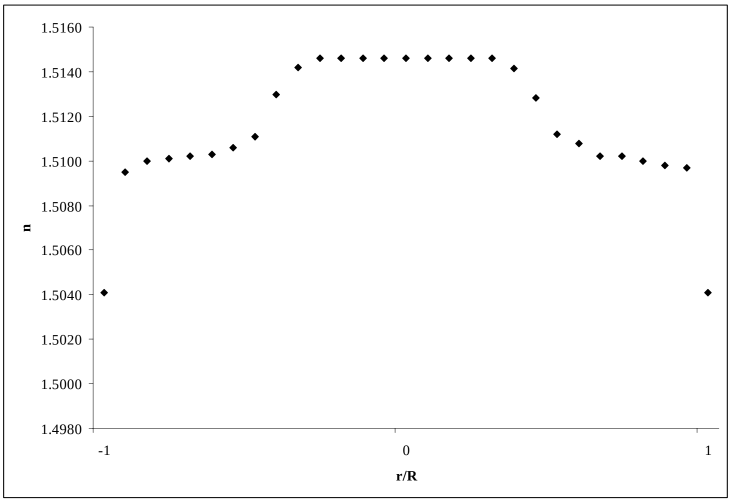

Figure 3. n profile with r/R_0.

The Figure 3 shows that the monomer is well diffused into the copolymer rod. The optical properties of the preform are dependent on this parameter (Δn shape) because $\Delta n(0)$ is directly related to the refractive index and the numerical aperture, and the Δn profile shape is closely related to the data transmission speed. Since the refractive index is linearly related to the concentration (copolymer composition) of the copolymer [11], the refractive index profile can be converted into a concentration profile. The $n(r/R_0)$ with r/R_0 is shown in Figure 4. Generally, the GI profile of the preform (core part) can be written as [12]:

$$n(r) = n_0\sqrt{1-2\Delta\left(\frac{r}{R_0}\right)^{\alpha}} \qquad (2)$$

Here r is the radial distance from the center of the preform, R_0 the radius of the preform, n_0 the refractive index at the center of the preform, n_1 the refractive index at the periphery of the preform and the dimensionless parameter α is defined as the index profile shape. The index difference (Δ) is defined as:

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

The transmission speed is highest when α is about 2 and Δ is 0.01 to 0.02 if there is no material dispersion [12-15]. The α and Δ values of the preform prepared under various experimental conditions are shown in Figure 4.

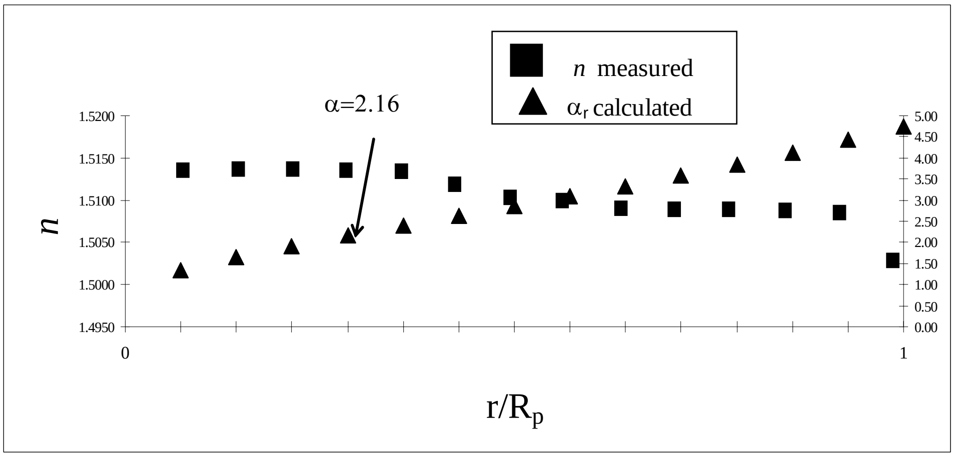

Figure 4. Refractive index profile with *r/R_p*. The square dot represents experimental data and the triangle represents calculated data by equation (2) with n_o = 1.5146, Δ = 0.00693, the best α = 2.16.

We compared α 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). It is clear that a smaller rod diameter requires a shorter heating time because the smaller rod separates from the axis more quickly. It is ease to predict that the α values of the preforms with a smaller diameter could have the same value with a lower diameter (Figure 5). Since the rod with the lower diameter has a thinner diffusion region (copolymer rod region), it reveals a smoother profile. Hence, the profile shape becomes smooth causing a favorable α value (i.e. 2.0) as the rod diameter decreases.

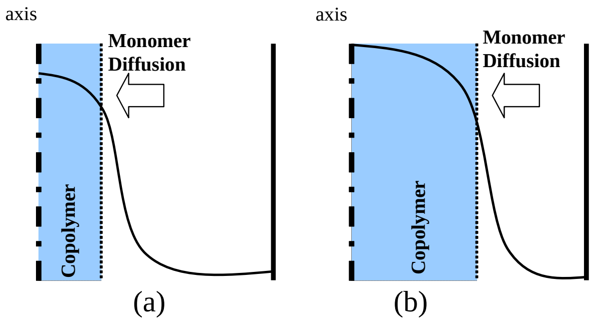

Figure 5. Schematic illustration on the formation of the refractive index profile shape. The rod diameters are (a) 2 mm and (b) 7 mm.

4. Conclusions

GI-POF preforms were successfully fabricated using the CFP method. The concentration fluctuation in the tangential direction was greatly reduced by a compositional controlled central polymer rod. The Δ and α values could be controlled by the copolymer rod diameter and composition. Namely, the Δ value increased with the PBzMA composition and the profile shape (α value) became smooth as the copolymer rod diameter decreased. 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.

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