Design and Fabrication of SCPOF Preform Doped with Rare Earth Complexes

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ABSTRACT: Segmented-cladding fibers (SCF) consist of a uniform core of high refractive index and a cladding with regions of high and low refractive index alternating angularly, which can effectively realize single mode with a large core diameter. Because polymer optical fibers are usually of large diameter, theoretical model for SCF was further extended to segmented-cladding polymer optical fibers (SCPOF) doped with rare earth complex in this article. On the basis of the physical principle, a material model for SCPOF was established, from which refractive index and glass transition temperature of polymer materials was predetermined for the core and cladding of SCPOF, respectively. According to the model, a preform for SCPOF was fabricated with the core doped with $Eu(DBM)_3Phen$ that has characteristic emission at 613 nm under excitation at 365 nm. From results of fluorescence photograph, it is clearly seen that the expected preform has been obtained by a two-step method developed in this work. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 111: 730–734, 2009

Key words: polymer optical fibers; photonic crystal fibers; segmented-cladding fibers; rare earth doped fibers

INTRODUCTION

Single-mode fibers (SMFs) made of silica have been used in long distance communication and many other applications.[1,2] Because it has no mode dispersion, SMFs can achieve high bandwidth and transmission rate. It is well known that silica SMFs are usually obtained with the very small core diameter (8 $\sim$ 6.25 μm) because of the high glass transition temperature of silica. Polymer optical fibers (POFs) have large core diameter (from 0.5 to 1 mm), and can be used in a short range communication network or a local area network (LAN) because they are easier in fiber connection that frequently be met within LAN.[3–6] At the same time, the large core diameter brought a problem of mode dispersion, which will results in attenuation of optical signal transmitting within the POFs. To decrease such a loss has attracted much attention in the field of POFs research, in which most successful attempt was development of graded index fibers (GI POFs).[7,8] The GI POFs has a well-adjusted refractive index distribution on its cross section, which can largely reduce mode dispersion. Photonic crystal POFs was also fabricated to overcome such a mode dispersion.[9–11]

A new design of fiber structure called segmented-cladding fiber (SCF) gave another way to fabricate SMFs, which has a uniform core of a high refractive index and a cladding with alternating angularly regions of high and low refractive indices.[12,13] For it's unique structure, especially for the single-moded operation realized in a large core diameter, application of SCF concept in POF has attracted much attention in recent years.[14–18] Under this circumstance, researches on the rare earth doped segmented-cladding polymer optical fibers (SCPOF) were started in our group based on our previous work on rare earth doped multi-mode POF.[19–28] In this work, a model for selection of suitable core and cladding polymers for SCPOF is proposed in terms of the physical principle and requirements for a preform of SCPOF. According to the model, a preform was prepared by a two-step method using polymers with pre-estimated refractive index and glass transition temperature.

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EXPERIMENT

$Eu(DBM)_3Phen$ was synthesized by following the procedure reported before.[29] Methyl methacrylate (MMA) and *n*-butyl methacrylate (*n*-BMA) were distilled under reduced pressure. 2, 2′-Azoisobutyronitrile (AIBN) was recrystallized from ethanol before use. *n*-octyl mercaptan (ACROS, 97%) was used as received.

The glass transition temperature of both high and low-index polymer was determined by DSC analysis (DSC-60, Shimadzu Corp.).

A SCPOF preform doped with $Eu(DBM)_3Phen$ was prepared by a two-step method. First, low-index polymer segments were made with a segment angle of 22.5 ± 2° by bulk polymerization within a mold composed of a glass tube and a copper cross-support that was used to controlling the segment angle; second, obtained low-index segments was fixed in another glass tube, and then, prepolymer with high-index containing $Eu(DBM)_3Phen$ with certain concentration was poured into the tube to perform bulk polymerization. After the polymerization, a SCPOF preform doped with $Eu(DBM)_3Phen$ was obtained.

A typical procedure for the preparation is described in details as follows. First, 130 mL of purified MMA, 400 μL of *n*-octyl mercaptan (as chain transfer agent), 20 mg of AIBN (as initiator), and 65 mg $Eu(DBM)_3Phen$, were mixed and filtered through a PTFE membrane filter (pore size: 0.2 μm). The above solution was heated to 80°C with stirring for about 120 min until it became rather viscous. The prepolymer fluid was cooled to room temperature, and then poured into a glass tube. After the fluid filled up about 10 cm height in the tube, a copper cross-support [see Fig. 6(a)] was inserted into the tube and totally immerged in the prepolymer fluid. Then the tube was sealed and again heated in an oil bath from 50 to 90°C at a heating-up speed of 5°C/12 h, then cooled to room temperature at the speed of 5°C/h. After breaking the tube, the low-index segments were peered off from copper cross-support. Second, 24 mL MMA, 16 mL *n*-BMA, 60 mg AIBN, and 100 μL *n*-octyl mercaptan were mixed and prepolymerized following the same steps described above. Four low-index segments were propped up in another glass tube by a small cross-support [see in Fig. 6(b)]. The cooled prepolymer fluid (high-index) was poured into the tube and filled into the cross-shaped space among the low-index segments. Tube was then sealed and also heated in oil bath from 50 to 130°C at a heating-up speed of 5°C/12 h, then cooled to room temperature at the speed of 5°C/h. Breaking the tube, a SCPOF preform doped with $Eu(DBM)_3$ Phen was obtained.

RESULTS AND DISCUSSION

Theoretical model of SCPOF with four segments

POF is usually of a large diameter, generally at about 1 mm. That makes it easier to launch optical power into the fiber and facilitates the connecting of similar fibers. Another advantage of the large core diameter is that light can be launched into the fiber with a light-emitting-diode (LED) source (cheaper), while laser diodes (much more expensive) is required for the normal SMF.[30] On the other hand, the large core diameter makes significant mode dispersion, which could cause pulse broadening and limit the bandwidth. To overcome this intrinsic character of POF, the concept of graded index POF was firstly introduced in 1980s, and many techniques have been developed to fulfill such a design. In recent years, a novel design was worked out,[31,32] in which segmented cladding was adopted as shown in Figure 1. From this figure it can be seen that in the core region ($0 < r < a$), refractive index is uniform (n_1); while in the cladding region ($a < r < b$), refractive indices alternate periodically and angularly ($n_1 > n_2$). In an optical fiber of such a structure with proper parameters, only fundamental mode can be transmitted along the fiber, and other higher modes will be leaked away by the cladding.[31,33]

It is well known that most used transmission window for POF is at 650 nm and refractive index is dependent on wavelength. Radial effective index method (REIM)[34] followed by the transfer matrix method[35,36] were used in this work to construct a SCPOF, and an effective-index profile $\tilde{n}_{effr}(r)$ of the fiber at the wavelength 650 nm was calculated by

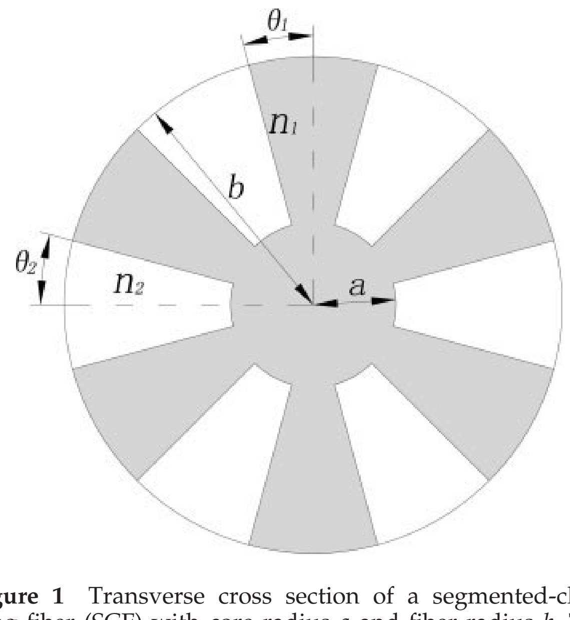

Figure 1 Transverse cross section of a segmented-cladding fiber (SCF) with core radius *a* and fiber radius *b*. The refractive indices of the segments are n_1 and n_2 ($n_1 > n_2$), and $2\theta_1$ and $2\theta_2$ are the corresponding angular widths.

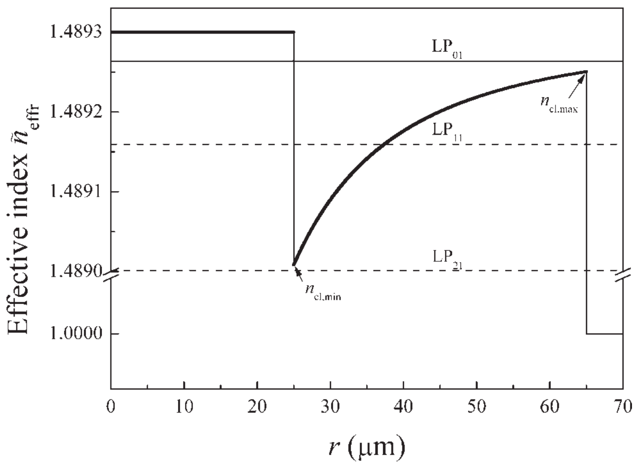

Figure 2 Effective-index profile of SCPOF with $a = 25$ μm, $b = 65$ μm, $\Delta = \frac{n_1^2 - n_2^2}{2n_1^2} = 0.0067$, at the wavelength 650 nm. $n_{cl,min}$ and $n_{cl,max}$ stand for lowest and highest effective-indices of cladding. The horizontal lines mark the mode indices of the first few modes of the fiber (blue solid line for LP_{01} mode, and dash lines for other high order modes).

using a tentative set of parameters from the work of material design presented in the next part.[37] The result is shown in Figure 2, and obviously, the effective-index profile is kept unchanging within the core when $r < a$ and varied monotonically with r from the minimum value $n_{cl,min}$ to the maximum value $n_{cl,max}$. The mode indices calculated for the first few modes are also shown in Figure 2. It is clear that only the mode index of the LP_{01} mode is larger than the maximum cladding index $n_{cl,max}$, while all the higher-order modes have mode indices smaller than $n_{cl,max}$. This suggests that only the LP_{01} mode is well guided by SCPOF and all other higher-order modes are cladding modes, which can be stripped off easily by using a suitable index-matching coating. As the result, the fiber is effectively single moded. Detailed geometrical data of our design is shown in Figure 5(a).

A map of RI and T_g of copolymers for SCPOF

It can be seen from discussion above that SCPOF requires a series of material parameters with precision, among which refractive index (RI) and glass transition temperature (T_g) are two key parameters. In a SCPOF construction, two kinds of polymers with different RIs are needed for core and cladding, respectively, which require precise preparation. Difference of RI between core and cladding is usually at the scale of $10^{-4} \sim 10^{-3}$. On the other hand, difference in T_g between core and cladding materials should be controlled, because it will affect fiber-drawing process. During the following design of SCPOF preform, the difference in T_g is pre-enacted as small as possible. However, it is difficult to meet such requirements at the same time for homopolymer. As a result, copolymers are considered for such a purpose, which are transparent at about 650 nm and have suitable RI and T_g. According to these principles, a map of RI and T_g for different copolymers has been constructed, from which a suitable pair of copolymers for core and cladding can be easily found by approximation degree of RI and T_g for two copolymers. At the same time, these data can be precisely obtained by calculation from following two equations[37,38]:

$$\frac{n^2 - 1}{n^2 + 2} = \frac{n_1^2 - 1}{n_1^2 + 2} x + \frac{n_2^2 - 1}{n_2^2 + 2} (1 - x) \quad (1)$$

$$\frac{1}{T_g} = \frac{x}{T_{g1}} + \frac{1 - x}{T_{g2}} \quad (2)$$

Figure 3 presents a typical example of such a map, showing part of results obtained from the calculation about poly(methyl methacrylate) (PMMA) and other acrylate polymers. From results in Figure 3, if PMMA, as one example, was adopted as the core material of SCPOF, the copolymers in the shadow region could be the candidates which meet the RI requirement. Meanwhile, based on T_g requirement, the copolymer candidates' T_g should be close to the MMA's. According to this method, one pair of copolymers was selected to construct a preform for SCPOF, in which the core polymer is PMMA doped with $Eu(DBM)_3Phen$, and the cladding polymer is p(MMA-*co*-*n*-BMA) with MMA content of 0.61. The DSC Analysis Results of PMMA and p(MMA-co-*n*-BMA) were shown in Figure 4. The T_gs of PMMA and p(MMA-*co*-*n*-BMA) were 114°C and 84°C, respectively. Both of

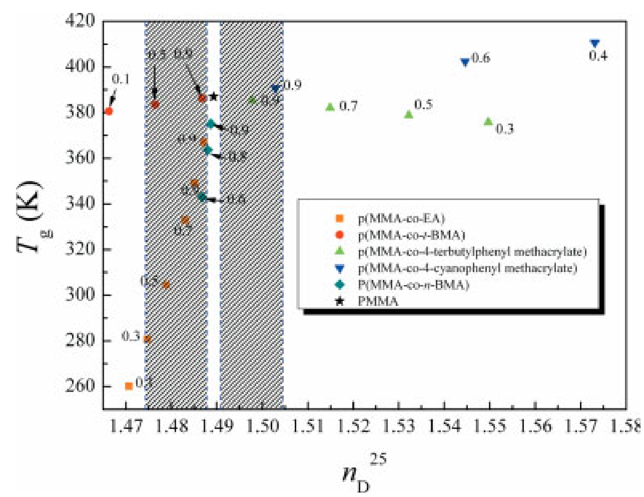

Figure 3 Relationship between T_g and refractive index of a series of copolymers composed of methyl methacrylate and other acrylates. Numbers represent weight fraction (w/w %) of methyl methacrylate in each copolymer. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

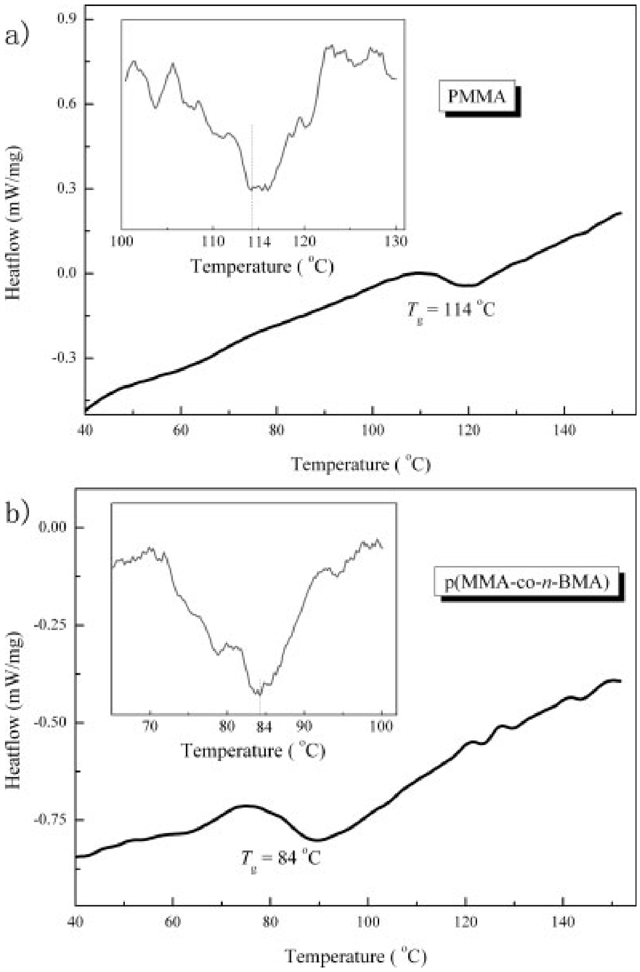

Figure 4 DSC analysis results of high-index material (PMMA) and low-index material (p(MMA-*co*-*n*-BMA)). The differential curves of heatflow are shown in the insert drawings, and their valley values give the transition temperatures.

the two T_gs were higher than the data given by Figure 3, and the difference between them was about 30°C, slightly smaller than the prediction. Effect of such a T_g-difference will be evaluated during the fiber drawing process, in which controlling of T_gs for core and cladding would be key point.

Preparation of SCPOF preform doped with $Eu(DBM)_3Phen$

Rare earth doped POF has been studied as it can be used as materials for fiber amplifier and laser.[19,20,39,40] However, it has been found that multimode fiber has lower efficiency than that of single mode fiber. Under this circumstance, a program concerning SCPOF doped with rare earth has been established after our previous work on multimode POF amplifie.[19,21–28]

Work presented here is concerned with preparation of a SCPOF preform doped with $Eu(DBM)_3Phen$ according to the design in Figure 5. The preparation was carried out in two steps. In the first stage, a copper mold [Fig. 6(a)] was fixed in a glass tube with a length of 30 cm and the inside diameter of 15 mm. The precopolymer with higher RI was obtained by bulk polymerization of the mixture of MMA and *n*-BMA at MMA content of 61%-w/w, and then poured into the tube to continue the polymerization till fully solidification. In this way, a wedge polymer stick with an angle of $67.5 \pm 2°$ was obtained, which will be used as high RI part of segmented cladding. In the second stage four of the wedge polymer sticks were fixed in another glass tube by an iron cross-fixer shown in Figure 6(b). The mixture solution of $Eu(DBM)_3Phen$ and pre-PMMA in MMA was poured into the tube, and the polymerization was carried out till fully solidification. According to theoretical calculation, concentration of $Eu(DBM)_3Phen$ was controlled lower than 0.2%-w/w, within which the change in RI caused by doping $Eu(DBM)_3Phen$ is limited within 10^{-4} scale, and there is no effect on the single mode property of SCPOF shown in Figure 2.

Figure 6(b) shows a picture of the cross section of SCPOF preform fabricated in the way described above, which was obtained by irradiating the cross section with light at 365 nm because $Eu(DBM)_3Phen$ has strong fluorescence at about 612 nm under the irradiation. It can be clearly seen from Figure 6(b) that there are four segmented areas on the cross section. An ideal SCPOF preform should be identical with the design shown in Figure 6(a), and can be further drawn into a fiber, which is still being carried out at present.

SUMMARY

The theoretical model of SCF was extended to POF, and rare earth containing SCPOF with four segmented areas was designed. To meet the requirement of the design in RI and potential requirement of fiber drawing in T_g for core and cladding

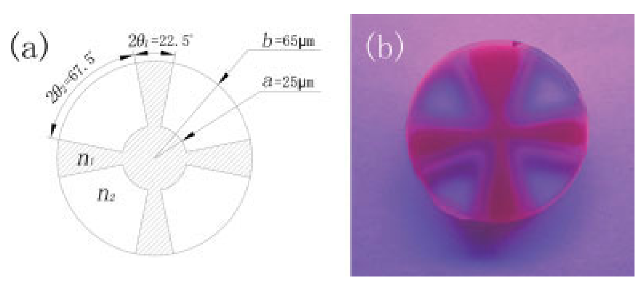

Figure 5 (a) Design of SCPOF with four segmented areas on cross section; (b) Photograph of the cross section of SCPOF preform with core doped with $Eu(DBM)_3Phen$. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

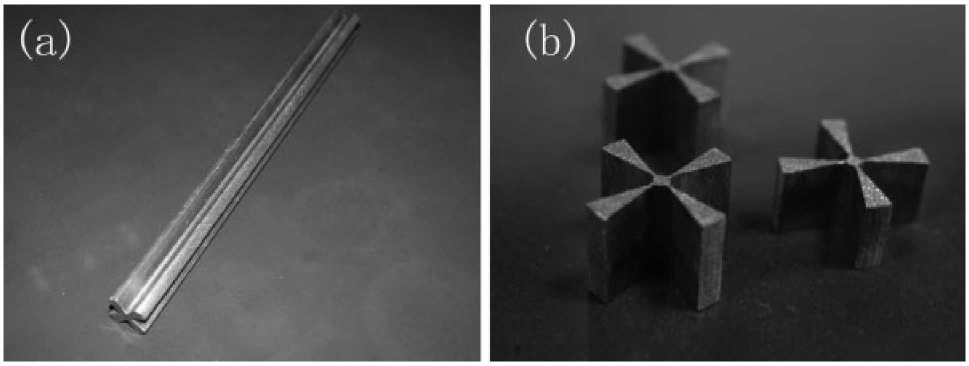

Figure 6 Photograph of copper mold (a) and iron fixer (b) used in preparation of SCPOF preform.

polymers, respectively, a map of $T_g \sim$ RI was established for a series of copolymers, from which a pair of suitable polymer can be convenient to be found out. As a result, PMMA doped with $Eu(DBM)_3Phen$ was used as core material, and p(MMA-*co*-*n*-BMA) with MMA content of 0.61 was used as cladding materials in this work, from which a SCPOF preform was fabricated by a two-step method. From the fluorescence picture of the preform's cross section, four segmented areas can be clearly seen on the cross section.

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