Preparation of Graded Index Plastic Rods Doped with Nd^{3+} by Interfacial-Gel Polymerization

QIJIN ZHANG, PIN WANG, YAN ZHAI

Department of Materials Science and Engineering, University of Science and Technology of China, Hefei, Anhui 230026, People's Republic of China

ABSTRACT: A novel graded index (GI) plastic rod was prepared by interfacial-gel polymerization carried out in a poly(methyl methacrylate) (PMMA) tube with one closed end. Bromobenzene (BB) was used to obtain a graded index distribution and neodymium octanate (NOA) as a dye with Nd^{3+} concentrations from 60 to 700 ppm. For a polymerization system containing methyl methacrylate (MMA) as monomers, azobisisobutyronitrile (AIBN) as an initiator, and dodecyl mercaptain as chain transfer agents, the difference of the refractive index from the center to the periphery of the rod (Δn) was found to be 0.015 at 18 wt % of BB and 60 ppm of Nd^{3+}. Experimental results also showed that a parabolic profile of refractive index formed on the cross section of the rod and Δn increased with BB contents increasing. NOA has little effect on the profile within the given concentrations. A description for forming the GI distribution is given by the free volume theory. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci **67:** 1431–1436, 1998

Key words: graded index; interfacial-gel polymerization; Nd^{3+}; diffusion in polymer

INTRODUCTION

Graded index (GI) polymers have recently attracted extensive attention in light of their highly promising potential in optical fiber communication[1] and polymer-based photonic integrated circuits.[2] For example, the whole bandwidth of GI polymer optical fibers (GI POFs) would be of the order of hundreds of megahertz that will be necessary in fast datalinks, short-range optical communications, and local area nets (LANs). However, all polymer optical fibers commercially available have been of the step-index (SI) type,[3] which bandwidth is only $\sim$ 5 MHz. GIPOFs are not only of high bandwidth, but also can be easily made with a large diameter, as to say, 0.5–1 mm, which is also necessary because many junctions and connections of optical fibers would be needed in short-distance communications and LANs.

On the other hand, in an optical communications system, as light passes along the fiber, the intensity of the light decreases due to various loss mechanisms. Besides other methods used to obtain low loss fibers, new techniques are based on amplifying the signal in fibers. One of the techniques is achieved by the optical signal extracting power indirectly from an optical pump, which is light-launched into a amplifying medium at a different wavelength from the signal. The amplifying medium is usually made into a fiber doped with one kind of dye and can be blocked into the optical system. When the fluorescence emitted from the dye has the same wavelength as the signal, an amplification is achieved. An Er^{3+} doped glass fiber amplifier has been developed in long-distance communication systems.[4]

Recently, organic dye-doped POF has been made and used as a fiber amplifier in LANs composed of POF. Tagaya et al. reported that polymer optical fiber amplifiers (POFA) of GI type were successfully prepared by the interfacial-gel polymerization technique.[5] In order to meet adequate

Table I   Characteristic Properties of Rods with Different PMMA/BB Ratio

PMMA/BB (wt/wt)	Nd^{3+} (ppm)	Δn	T_g (K)
10 : 1	60	0.0053	373.5
7 : 1	60	0.0085	371.7
5 : 1	60	0.0145	369.4
3 : 1	60	/	364.2

T_g is calculated from the equation of the polymer–plasticizer system.[8] T_g of PMMA (378 K) can be obtained from ref. 6, volume thermal expansion coefficient of PMMA (2.25×10^{-4} K^{-1}) can be obtained from ref. 9, and volume thermal expansion coefficient of BB (0.97×10^{-4}) can be obtained from ref. 10.

solubility in the chosen polymer bulk, rhodamine B was chosen as the dye in the fiber amplifier. It was shown that neodymium octanate (NOA) is soluble in poly(methyl methacrylate) (PMMA) and Nd^{3+}-doped PMMA can be made into SI fibers.[6] In order to make Nd^{3+}-doped GI POF, Nd^{3+}-doped GI PMMA rods were prepared first. The interfacial-gel polymerization was used in the presence of NOA. The mechanism of forming GI distribution and the effects of NOA and BB on the values of Δn were discussed.

EXPERIMENTAL

Materials

NOA was synthesized at our laboratory according to the reported procedure.[7] Tubes of PMMA are commercial samples produced by Xingguang Chemical Regent Factory in Beijing, with 6-mm inner diameter and 10-mm outer diameter. The other chemicals and solvents were commercial products and used after purification in terms of standard methods.

Polymerization

The PMMA tubes were sealed on one end and then filled with a solution composed of methyl methacrylate (MMA) as a monomer, azobisisobutyronitrile (AIBN, 0.01 mol/L) as an initiator, dodecyl mercaptan (0.03 mol/L) as a chain transfer agent, and specified amounts of bromobenzene (BB) and a 60 μL solution of NOA in acrylic acids. The composition of the mixed solution for each experiment is listed in Table I. The PMMA tube was placed into a glycerin bath with a constant

temperature of 80°C for 1 h, and then 70°C until the solidification was fulfilled. After the solidification, the tube was placed into a vacuum oven at $\sim$ 100°C for 2 h, and then a preformed rod was ready for use as a sample in this work.

Characterization

The refractive index was measured by the oil immersion method. A series of matching oils were used with the Δn of two adjacent oils being 0.003. Samples were prepared by cutting on the cross section of the preform rods, the diameter of which is $\sim$ 0.1 mm. The sample was then placed on one side of a glass sheet and covered by a small piece of micro cover glass. A drop of matching oil was dripped and diffused over the sample. The refractive index was determined by the beckeline method on an Olympus polarization microscope. The accuracy of this measurement was in the range of $\pm$0.0015.

RESULTS AND DISCUSSION

It is known that there are two methods for preparing POF. One is called the fiber-drawing method, which is often used to make SIPOF, although a new similar method, by extrusion, has developed for GIPOF recently[11]; another one is for GIPOF and includes two steps: the first step is preparing preforms—a rod with a graded index distribution on the cross section—and the second is drawing a fiber from the rod while heating it. The first step is more concerned with polymer chemistry, and there have been several techniques developed in recent years, for example, two-stage copolymerization,[12] photocopolymerization,[13] centrifugal molding,[14] interfacial-gel copolymerization,[15] and vapor phase diffusion copolymerization.[16] Especially for making GIPOF amplifier, a dye-doped preform was synthesized by interfacial-gel polymerization in which rhodanmin B (RB) was used as the dye.[5] When a rare earth compound is used instead of RB, compatibility between the compound and polymers is the first factor needed to be considered. NOA was found to be soluble in MMA and compatible with PMMA in a previous article[6] and was used as a dye in this article.

Different from interfacial-gel copolymerization, interfacial-gel polymerization used in this article is a homopolymerization process in which a PMMA tube is filled with an MMA monomer mixture with polymerization initiator, the chain
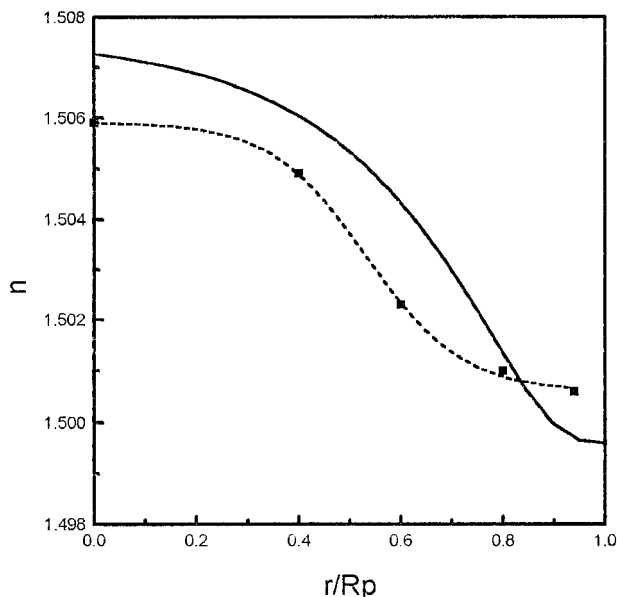
Figure 1 Refractive index distribution of Nd^{3+}-doped PMMA preform: (-----) experimental results; (——) theoretical simulation.

transfer agent, and one kind of molecule inert to the polymerization.[17] A gel layer forms on the PMMA tube inner wall when PMMA is partly dissolved in the mixture; the thickness depends upon many factors, including swollen time before the polymerization, temperature, and the properties of PMMA tube used. In the gel layer, when polymer contents are within 20–80%, polymerization would be faster due to the gel effect (an autoacceleration in the polymerization rate as the reaction proceeds) than in the polymer content >80% part, which is closer to the tube inner wall, and in the polymer content <20% part, which is close to the center region of the tube. With the polymerization continuing, the gel layer will gradually thicken to the center region and a gradient polymer concentration distribution forms at the radial direction of the tube. At the same period, the inert molecule and MMA will gradually be distributed with a concentration gradient contrary to the polymer concentration gradient in the gel layer. This concentration distribution is formed by equilibrium between the formation of polymers and diffusion of small molecules before full solidification of the gel layer, and results in a graded index distribution when the inert molecule has a refractive index different from that of polymers. Bromobenzene (BB, $n = 1.56$) was selected to use as the inert molecule in our experiment, and the result is shown in Figure 1(a), from which it can be seen

that the preformed rod has a parabolic profile of refractive index with the highest refractive index value at the center of the rod, and a cladding region that comes from the PMMA tube. The result of Figure 1(a) also shows that swollen time is suitable at given PMMA tube and temperature, but also shows that the PMMA tube was deformed when the swollen time was too long.

Generally speaking, for forming the graded index distribution, the inert molecule has to satisfy two conditions: higher refractive index and the same compatibility to the PMMA as that of MMA. BB has a higher refractive index (1.56) than that of MMA (1.42).[18] Although no data of the compatibility are available for BB and MMA, we found that two chemicals can mix at any concentration and the molecular sizes for BB and MMA are approximately identical ($d = 6.9$ Å) according to calculation in terms of densities. It has been also reported that the calculated solubility parameters are 7.814 $(cal/cm^3)^{1/2}$ and 8.468 $(cal/cm^3)^{1/2}$ for MMA and BB, respectively.[19] When the gel layer formed, a gradient PMMA concentration exists at the vertical direction of the gel layer, which resulted from a mutual diffusion process of PMMA and the mixture solvents. At the same time, a gradient BB concentration also formed in the same direction. Because of the gel effect which results in a higher rate of gel layer thickening than the rate of the full solidification of the layer, the gel phase would reach the center of the tube with a gradient distribution of PMMA concentration on the cross section of the tube before the gel is fully solidified. At this time, a diffusion equilibrium between PMMA and small molecules reached and the equilibrium state can be described by the free volume theory.

According to the Vrentas–Duda model of small-molecule diffusion in polymer concentrated solutions, the diffusion coefficient depends on temperature and concentrations of polymer and small molecules. The equation can be expressed as[20]:

$$\ln D_1 = \ln D_0 - \frac{E}{RT}$$
$$- \left[- \frac{(1 - \omega)\hat{V}_1^* + \omega\xi\hat{V}_2^*}{\hat{V}_{FH}/\gamma} \right] \quad (1)$$

$$\hat{V}_{FH}/\gamma = (1 - \omega)\left(\frac{K_{11}}{\gamma}\right)(K_{21} + T - T_{g1})$$
$$+ \omega\left(\frac{K_{12}}{\gamma}\right)[K_{22} + \alpha(T - T_{g2})] \quad (2)$$

Table II   Vrentas–Duda Free Volume Parameters

	MMA	Reference	BB	Reference
$\hat{V}_1^*$ (cm^3/g)	0.87	21	0.591	24
$\hat{V}_2^*$ (cm^3/g)	0.757	21	0.757	24
$(K_{11}/\gamma) \times 10^3$ (cm^3 g^{-1} K^{-1})	0.815	21	0.64	—[a]
K_{21} (K)	143	21	184.6	—[a]
$(K_{12}/\gamma \times 10^3$ (cm^3 g^{-1} K^{-1})	0.477	21	0.477	—[a]
K_{22} (K)	52.38	21	52.38	—[a]
T_{g1} (K)	143	21	242.4	24
T_{g2} (K)	378	6	378	6
α	0.44	21	0.44	21
D_0 (cm^2/s)	4.07×10^{-5}	—[a]	1.92×10^{-5}	—[a]
E (Cal/mol)	0	22	0	22
ξ	0.60	21	0.60	21

[a] Calculated from the temperature dependence of MMA viscosity in ref. 23 and BB viscosity in ref. 24.

where the small molecule is component 1 and the polymer is component 2. Also, D_0 is an effectively constant preexponential factor, E is active energy, $\hat{V}_i^*$ is the specific hole free volume of component i required for a jump, ω is the mass fraction of polymer, T is the temperature, T_{gi} is the glass transition temperature of pure component i, ξ is a size parameter which is the ratio of the critical molar volume of the small molecule jumping unit to the critical molar volume of the polymer jumping unit, $\hat{V}_{FH}/\gamma$ is the solution free volume, and (K_{11}/γ), K_{21}, (K_{12}/γ), and K_{22} are free volume parameters.

The Vrentas–Duda free parameters of MMA and BB are listed in Table II. The dependence of D_{MMA} and D_{BB} on polymer concentration at 80°C are obtained according to the procedure detailed in ref. 20 and illustrated in Figure 2. It was veri-
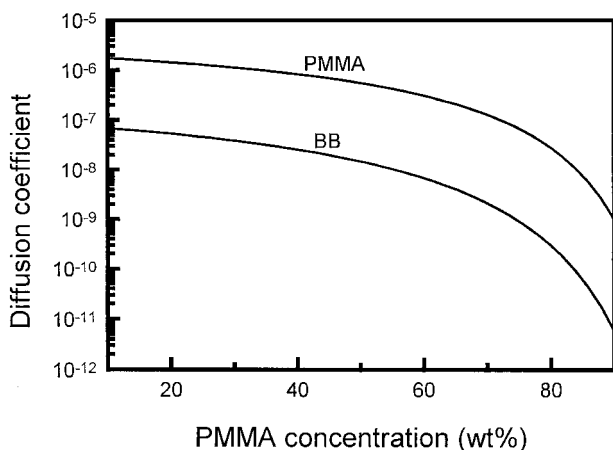
Figure 2 Values of D_{MMA} and D_{BB} as a function of PMMA concentration at 80°C.
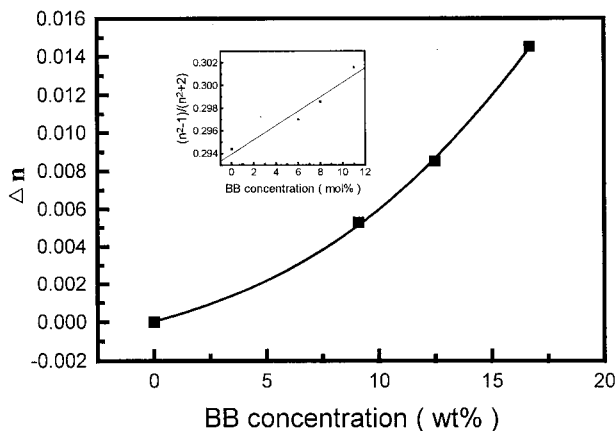
fied that D is independent of PMMA molecular weight,[21] so the D_{MMA} and D_{BB} values displayed in Figure 2 include the data for all the PMMA molecular weights. Also, since the PMMA concentration at which the solution becomes glassy was estimated as 93% at 80°C,[21] the Vrentas–Duda model, in the form of eqs. (1) and (2), is valid within the concentration range available in Figure 2. The results in Figure 2 show that changing tendencies of D_{MMA} and D_{BB} values with PMMA concentrations are identical, and D_{MMA} is slightly larger than D_{BB}, which comes mainly from the difference of correspondent D_0 values list in Table II calculated from MMA and BB viscosities, respectively.

Assuming that there is no interaction between MMA and BB molecules, from the data of D_{MMA} and D_{BB} refraction index distributions can be simulated by one procedure developed in our lab[25] [Fig. 1(b)]. In the procedure two conversions were used: one for D to concentration is fulfilled by the first Fick's law, and another for concentration to refractive index is completed according to the Lorentz and Lorenz relationship (Fig. 3, inset). The curve of Figure 1(b) is in reasonable agreement with the values of refractive index obtained experimentally. This result shows that the process for forming the parabolic profile of refractive index is diffusively controlled, and the relationship between two diffusive coefficients of the monomer and the inert small molecules is a key factor in determining the distribution of refractive index on the cross section of the preform.
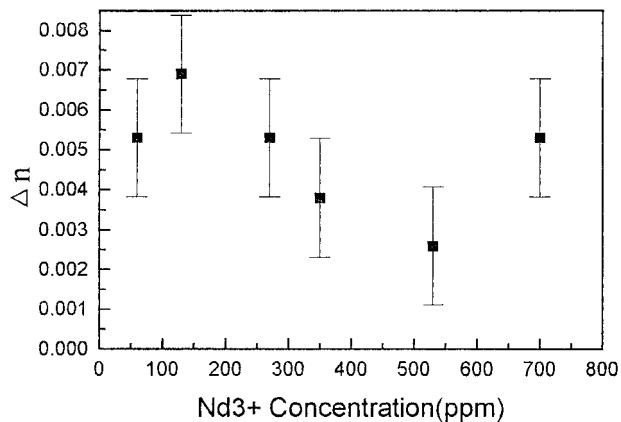
Absolute Δn values between the center of the rod and a cladding region is ~ 0.005 for an Nd^{3+}-

doped PMMA rod at the ratio of MMA/BB = 10 : 1 from Figure 1(a), and similar to the value of an RB-doped PMMA rod at the same ratio of MMA/BB.[18] It can be found from Figure 3 that the value increases with increasing of BB contents. For the compatibility system, the relationship between refractive index and compositions of the system can be theoretically correlated by the Lorentz and Lorenz formulation,[26] that is, $(n^2 - 1)/(n^2 + 2)$ and C_{BB} should have a direct-proportion relationship. The inset in Figure 3 has shown the results calculated from the experimental data for preforms with different BB concentration. A solid line was fitted by the least-square method and the correlation coefficient is 0.97. It is worth noting that the same distribution of refractive index for different BB contents was found in this system as reported before.[18] This is identical with our analysis mentioned above. It has also been found in this article that the PMMA rod has shown flexibility when the ratio of MMA/BB < 3 : 1 and is hard to use in the preparation of GIPOF. This results from plasticizing actions of BB in PMMA according to the free volume theory. T_g of the plasticization system has been given in Table I and shows a decrease with increasing BB contents.

Figure 4 has shown the relationship between Nd^{3+} content and Δn values at a fixed ratio of MMA/BB = 10 : 1. The result shows that Δn values can be considered nonchanging within the accuracy range of ±0.0015 as the concentration of Nd^{3+} has increased >10 times. This may be due to the absolute concentration of NOA within 0.3 wt %, although it has increased >10 times during

Figure 4 Effects of Nd^{3+} concentration on Δn values of Nd^{3+}-doped PMMA preform.

this work, while that of BB is 9.1 wt % for the system of MMA/BB = 10 : 1. On the other hand, NOA is in the solid state at 80°C and is a molecule with a long aliphatic chain. During the polymerization it is easily dissolved in the reactive mixture as it has good compatibility with PMMA and other components.[6]

CONCLUSIONS

A novel Nd^{3+}-doped preform for making GIPOF has been obtained by interfacial-gel polymerization. A parabolic profile of refractive index with the highest refractive index value at the center of the rod can be found on the cross section of the rod. Its forming mechanism has been analyzed in detail and simulated using the Vrentas–Duda model. The result shows that viscosity and concentration of the inert molecules are two key factors determining the gradient of refractive index of the preform. Effects of NOA with small concentration on GI distribution has also been examined and no sensible influence has been found in this system.

Figure 3 Relationship between Δn and bromobenzene concentration. Inset shows a correlation of the same data formulated by the Lorentz and Lorenz relationship.

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