Preparation of Gradient-Index (GRIN) Polymer Fibers for Imaging Applications

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SYNOPSIS

A closed extrusion process combined with a core-shell separation die design is developed in this study for preparing gradient index (GRIN) polymer fibers with a quadratic distribution of the refractive index. The material system used in this investigation is methyl methacrylate (MMA, $n = 1.49$) and benzyl methacrylate (BzMA, $n = 1.568$). The refractive index differences between the center and the periphery (Δn) of the prepared polymer fibers increase from 0.0115 to 0.020 when BzMA in the reactant mixtures increases from 17 to 28%. This finding would suggest that increasing the high refractive index monomer in the reactant mixture increased Δn. The Δn values decrease from 0.018 to 0.0135 when the diffusion zone temperature increases from 70 to 90°C. The diffusion rates of the monomers increase with the temperature, thereby causing BzMA and MMA to distribute more uniformly at a higher temperature than at a lower one. This uniform distribution leads to the decrease of Δn with an increasing temperature. The prepared GRIN polymer fibers have potential applications as imaging lenses for scanners, fax machines, and copiers. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Gradient-index (GRIN) materials with the refractive index varying continuously have attracted extensive interest in light of their versatile applications in imaging, collimating, and optical communications.[1-6] They have been used as the essential components of the selfoc lens array (SLA), which is currently used in the imaging parts of commercially available fax machines. They have also been used in medical endoscopes, copiers, scanners, fiber optical couplers, and camera elements.

A relatively new application of GRIN polymers is in the area of optical fiber communication. Koike et al. obtained a GRIN polymer optical fiber (POF) with a low optical loss and high bandwidth, which transmitted a 2.5 Gb/s signal over 100 m by using a 647-nm high speed laser diode.[3] Hence, GRIN POFs have been recommended for use in a high speed multimedium network.[3] Another potential application of GRIN POF would be as an optical fiber amplifier by doping with organic dyes.[7] Ishigure et al.[8,9] demonstrated that GRIN POF doped with rhodamine B is a high gain (27 dB for 0.5-m optical fiber), high energy conversion efficiency (more than 60%), and high power (420 W) optical amplifier at 591 nm.

GRIN polymer fibers were conventionally prepared by extrusion processes.[10-13] Our previous study successfully used a closed extrusion process to prepare GRIN polymer fibers.[13] This new process has overcome several drawbacks presented in conventional extrusion processes, for example, the difficulties encountered in selecting optimum conditions, poor reproducibility because of the gas blowing in the diffusion zone, and the long diffusion time required that subsequently resulted in a long manufacturing time and low production rate. However, the polymer fibers prepared by the closed extrusion process reported in our previous study had only a 62% quadratic refractive index distribution.[13] This would not be suitable for imaging applications, which require a completely quadratic refractive index distribution.

In this study, a closed extrusion process combined with a core–shell die design is developed to prepare

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GRIN polymer fibers with a complete quadratic distribution of the refractive index. The nonquadratic index portion of the polymer fiber is cut by the core–shell separation die. Hence, the prepared GRIN polymers would be suitable for imaging applications. The material systems used in this investigation are the host polymer, poly(methyl methacrylate) (PMMA), along with the monomers methyl methacrylate (MMA) and benzyl methacrylate (BzMA). Moreover, the effects of the reactant formulations and the diffusion zone temperature on the refractive index distributions are also examined. Furthermore, the BzMA and MMA compositions inside the fiber and the distribution constant A are estimated according to the refractive index distribution. The refractive index varies within the GRIN cylindrical material as shown in the equation:

$$n(r) = n_c(1 - \tfrac{1}{2}A(r/R_p)^2) \quad (1)$$

where n_c and $n(r)$ are the refractive indices at the center axis and at the distance r from the center, respectively, R_p is the radius of the fiber, and A is the distribution constant.

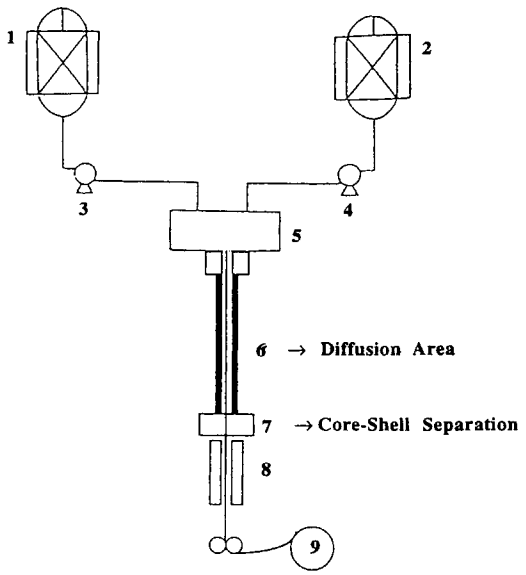

Figure 1 Experimental setup of the closed extrusion process for preparing GRIN polymer fibers. 1 and 2, material supply tanks; 3 and 4, gear pumps; 5, a concentric die; 6, an enclosed zone; 7, a core-shell separation; 8, a hardening zone; 9, rolls.

EXPERIMENTAL

Materials

MMA (99%, Janssen Chimica) and BzMA (98%, TCI) were purified by vacuum distillation. PMMA1 (Chi-Mei, Co., M_w 8.3×10^4, M_n 4.0×10^4), PMMA2 (Asahi, DELPET 70H, M_w 13×10^4, M_n 8×10^4), 1-hydroxycyclohexyl phenyl ketone (HCPK, TCI), and hydroquinone (HQ, 99%, Janssen Chimica) were used without further purification. The MMA and BzMA monomers have similar reactivity ratios and the refractive indices of their homopolymers were 1.490 and 1.568, respectively. The diffusion coefficients of MMA and BzMA in PMMA measured by Pulsed-Gradient Proton NMR (33MHz) were too close to be distinguishable (Prof. von Meerwall, Univ. of Akron, Akron, OH).

Preparation of GRIN Polymer Fiber

The closed extrusion process for preparing GRIN polymer fibers was described in our previous investigation.[13] In this study, a core–shell die design was used to modify the diffusion zone of the closed extrusion process as described below. Figure 1 shows a schematic diagram of the apparatus of the extrusion process used for preparing GRIN polymer fibers. A material supply tank (1) contained the solution of a polymer (A) and at least one monomer (B) [may have contained another monomer (C)]; meanwhile, a material supply tank (2) contained the solution of a polymer (D) and at least one other monomer (E). These two solutions were heated at 60°C. Next, gear pumps (3) and (4) with a speed of 0.5 and 1.5 mL/min were used to feed the two reactant mixtures 1 (core) and 2 (shell) with the volume ratio of 1 : 3 into a concentric die (5), respectively. Next, a dual-layer composite fiber was extruded out of the orifice of the die and fed into an enclosed zone of 45 cm (6), which was maintained at a constant temperature. While the fiber went through the diffusion zone, the monomer B and/or C in the inner layer and the monomer E in the outer layer diffused into each other, subsequently producing the effect of a continuous distribution of refractive index in the fiber. At the end of the diffusion zone, the fiber was extruded through a smaller orifice and 40% of the outmost portion of the fiber was removed through a core–shell separation die design (7). The fiber was then fed through a hardening zone (8) where it was hardened by four UV lamps of 60 W/cm each. Thus, a polymer fiber with a parabolic distribution of refractive index was taken up through rolls (9) by a take-up roll. The formulations of the reactant mixtures **I–III** are listed in Table I. Two different kinds of PMMA polymers, i.e., PMMA1

Table I Formulations of Reactant Mixtures I–III for Extrusion Process

	I	II	III
Mixture 1 (core)			
PMMA1 (%)	32	32	58
PMMA2 (%)	25.5	25.5	0
BzMA (%)	17	20	28
MMA (%)	25.5	22.5	14
HCPK (%)[a]	0.5	0.5	0.5
HQ (ppm)[b]	50	50	50
Mixture 2 (shell)			
PMMA1 (%)	29	29	60
PMMA2 (%)	26.4	26.4	0
MMA (%)	44.6	44.6	40
HCPK (%)[a]	0.5	0.5	0.5
HQ (ppm)[b]	50	50	50

[a] The weight ratio of photoinitiator HCPK over (polymers + monomers).

[b] The weight ratio of inhibitor HQ over (polymers + monomers).

and PMMA2, were used for adjusting the viscosity of the reactant mixtures suitable for gear pumps in the extrusion process. Polymers fibers **I–III** were prepared from the reactant mixtures **I–III**, respectively.

Characterization

The refractive index profile of the prepared GRIN polymer fiber was measured using a Jenaval interphako interference microscope (Carl Zeiss Jena Gumb), in which a matching oil with a refractive index of 1.492 was used as the reference. The instrument accuracy was in the range of ±0.0002. The polymer thin film for the measurement of the refractive index distribution was then prepared by cutting the polymer fiber using a Microtome HM 350 (Microm GmbH). The film thickness was 30 μm. The polymer film was then placed on the slide and covered by a small piece of micro cover glass. A drop of embedding liquid was then placed on the slide, and the oil was diffused all over the surface of the micro cover glass. The relationships between Δn, (r/R_p), and $(r/R_p)^2$ were fitted by quadratic curve-fitting and straight line-fitting methods, respectively. Where r is the distance from the center of the fiber, R_p is the radius of the fiber, and Δn is the difference of the refractive index at distance r and at periphery (n_p). The determination coefficient (k^2) of the line fitting was calculated according to Chapra and Canale.[14] The closer k^2 approaches 1, the more accurate the fitting. The distribution constant A was determined from the curve fitting of Δn with $(r/R_p)^2$.

RESULTS AND DISCUSSION

Preparation of Polymer Fibers with Completely Quadratic Index Distribution

Our previous study indicated that various factors could affect the refractive index distribution of the GRIN polymer fiber in the closed extrusion process, for example, the molecular properties of monomers such as refractive index and diffusivity and the operating parameters of the diffusion process such as diffusion length and temperature of the diffusion zone and the feeding speed of the gear pumps.[13] That study also revealed that following the completion of the diffusion process of monomers B, C, and E, the outermost layer of the polymer fiber no longer exhibited a refractive index distribution that conformed to a quadratic parabolic curve, even after the optimization of the types of the monomers, the length, and the temperature of the diffusion zone. In this study, a core–shell separation die design was used to cut out the nonimaging portion, that is, the nonquadratic distribution of the refractive index. Therefore, a GRIN polymer fiber with a complete quadratic refractive index distribution could be obtained.

Two approaches to cut out the nonimaging portion of the polymer fiber are removing the nonimaging layer of the polymer fiber before it is UV cured and removing the nonimaging portion after it is UV cured. Both approaches can obtain smooth and transparent polymer fibers. In this study, the first method was used through a special die design shown in Figure 1.

Effect of Reactant Formulations on Refractive Index Profiles

Figure 2 shows the relationships between Δn and (r/R_p) of the polymer fibers **I–III** from the extrusion process combined with the diffusion zone temperature at 90°C. The quadratic curve fitting of the refractive index profiles for polymer fibers **I–III** had the determination coefficients (k^2) of 0.99513, 0.99526, and 0.99147, respectively. Because the values of k^2 are very close to 1, the refractive index profiles for polymer fibers can be regarded as a quadratic distribution. This result implies that the nonquadratic index portion was removed by the core-shell separation process and the obtained GRIN

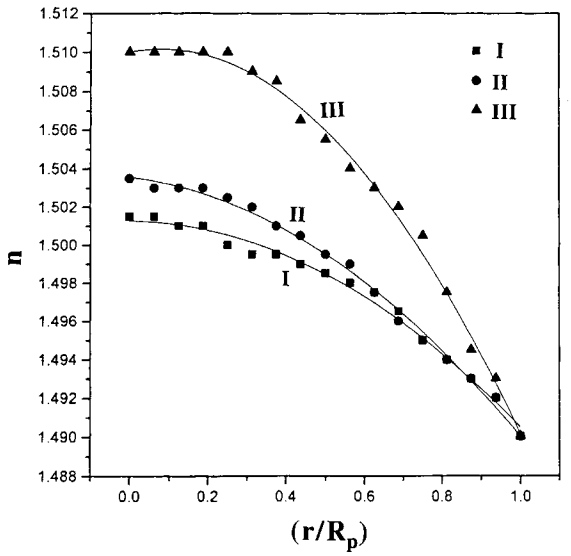

Figure 2 Relationships between the refractive index (n) with (r/R_p) of polymer fibers **I–III** prepared from the extrusion process with the diffusion zone temperature at 90°C.

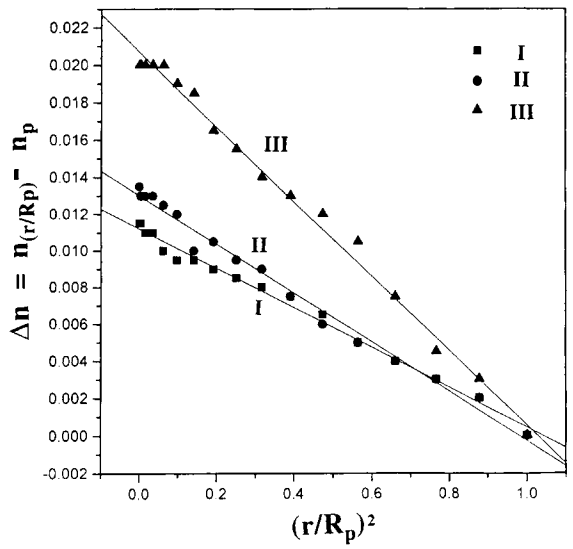

Figure 3 Relationships between the difference of the refractive index Δn with $(r/R_p)^2$ of polymer fibers **I–III** prepared from the extrusion process with the diffusion zone temperature at 90°C.

polymer fibers have potential applications as imaging lenses.

The values of k^2, n_c, n_p, Δn, and A determined from curves **I–III** in Figure 2 are listed in Table II. The quadratic distribution of the refractive index suggests that the mutual diffusion of MMA and BzMA occurred in the diffusion zone and resulted in a distribution of different MMA and BzMA compositions inside the fiber. The Δn values of polymer fibers **I–III** were 0.0115, 0.0135, and 0.02, respectively. This result indicates that increasing the high refractive index monomer BzMA in the reactant mixtures increases Δn. Because the refractive indices of PMMA and PBzMA are 1.490 and 1.568, respectively, the compositions of the centers of the polymer fiber contain 14.7, 17.3, and 25.6% of BzMA for the reactant mixtures **I–III,** respectively. Figure 3 shows the line fitting of the relationship between Δn and $(r/R_p)^2$ for polymer fibers **I–III.** The distribution constants A of polymer fibers **I–III** calculated from the slopes of the fitted lines were 1.41×10^{-2}, 1.75×10^{-2}, and 2.65×10^{-2}, respectively.

Table II Values Calculated From Refractive Index Distributions of Polymer Fibers I–III

	k^2	n_c	n_p	Δn	A
I	0.99513	1.5015	1.490	0.0115	1.41×10^{-2}
II	0.99526	1.5035	1.490	0.0135	1.75×10^{-2}
III	0.99147	1.510	1.490	0.02	2.65×10^{-2}

Effect of Temperature of Diffusion Zone on Refractive Index Distribution

Figure 4 shows the refractive index distribution of the polymer fibers prepared from the reactant mixtures **II** with the diffusion zone temperatures at 70, 80, and 90°C, respectively. The Δn values calculated from curves **IV–VI** were 0.018, 0.016, and 0.0135, respectively. The diffusion rates of the monomers

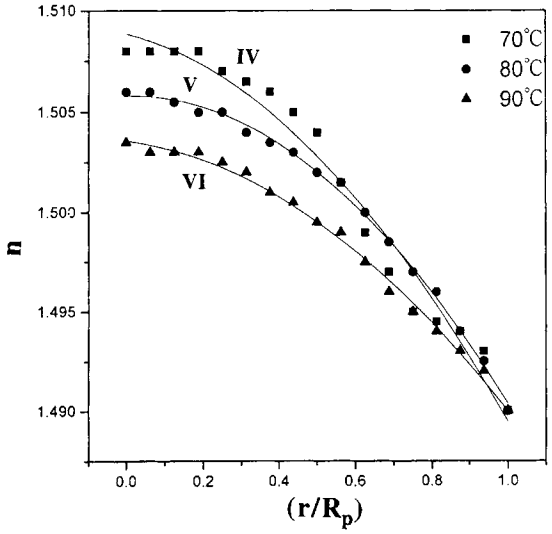

Figure 4 Relationships between the refractive index (n) with (r/R_p) of the polymer fibers prepared from reactant mixture **II** by the extrusion process with the diffusion zone temperature at 70, 80, and 90°C, respectively.

increased with an increasing temperature. Thus, BzMA and MMA inside the polymer fiber distributed more uniformly at a higher temperature than at a lower one. This uniform distribution subsequently led to the decrease of Δn with an increasing temperature.

CONCLUSIONS

GRIN polymer fibers with a completely quadratic refractive index distribution were successfully prepared in this study by a closed extrusion process via a core-shell separation die design. The nonquadratic index portion of the GRIN polymer fiber was cut out through the separation process. Experimental results revealed that the refractive index profiles of the prepared polymer fibers were significantly affected by the reactant formulations and the diffusion zone temperature. The Δn values increased with increasing high refractive index monomers in the reactant mixtures. Furthermore, the values of Δn decreased with increased diffusion zone temperature. The obtained GRIN polymer fiber has potential application as an imaging lens.

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