

# NOTES

## Studies on the Preparation of Gradient-Index Polymeric Rods by Interfacial-Gel Copolymerization

### INTRODUCTION

Scientific interest in gradient-index (GRIN) polymers has grown rapidly because of their potential applications in local area networks (LAN), imaging systems, and light guides.<sup>1</sup> The GRIN polymer optical fiber has been demonstrated to have a bandwidth of 2 GHz km and also a low optical loss of 56 dB/km at 688 nm wavelength.<sup>2</sup> Hence, they can be used in high-density optical fiber communication, where the bandwidth of 500 MHz km is required. Mitsubishi Rayon Co. of Japan has already commercialized a selfoc lens array (SLA) for the image transfer of fax machines, in which SLA was made of GRIN polymeric lenses.

The refractive index varies within the GRIN cylindrical material as shown in eq. (1):

$$n(r) = n_c(1 - 1/2A(r/r_p)^2) \quad (1)$$

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 rod; and  $A$  is the distribution constant. The unusual distribution of the refractive index of GRIN materials causes them to have quite different characteristics from the conventional step-index (SI) materials. Light travels through the GRIN medium in sinusoidal fashion without coming into contact with the wall, while the SI medium relies on the internal reflection at the walls. Also, the propagation velocities of various modes in SI medium differ, but those are the same as in the GRIN medium.

Several synthetic methods have been used to prepare GRIN plastic rods.<sup>1</sup> In those investigations, the differences among the monomer concentrations, monomer reactivities, and monomer sizes are the driving forces behind producing the index gradient inside the polymers. In this study, the interfacial-gel copolymerization method proposed by Koike et al.<sup>2-8</sup> is of priority concern because of the advantage of monolithical fabrication over other methods. This technique allows for preparing different shapes of GRIN rods, e.g., Y-branching and the lens array to be made directly from the interfacial-gel copolymerization. Koike et al. suggested the requirement for pro-

ducing GRIN materials by interfacial-gel copolymerization. Two monomers with different indices ( $n_1 < n_2$ ) should satisfy the following conditions: (a)  $r_1 > 1$  and  $r_2 < 1$  such as methyl methacrylate (MMA) with vinyl benzoate (VB) or (b)  $r_1 = r_2 = 1$  and the size of  $M_1$  is less than  $M_2$  such as MMA with benzyl methacrylate (BzMA).<sup>\*</sup> In this method, different reaction conditions, i.e., initiator, chain-transfer agent, and reaction temperature, can affect the formation of defects such as bubbles and mistiness and the difference of the refractive index ( $\Delta n$ ) between the center and the periphery of the GRIN rod.

In this study, the effects of the reaction conditions, i.e., the amounts of initiator and chain-transfer agent and temperature, on the formation of the defects and the  $\Delta n$  of the GRIN rods were studied. The monomer system used was MMA with BzMA. Benzyl peroxide (BPO) and *n*-butyl mercaptan (*n*BM) were used as the initiator and chain-transfer agent, respectively. The effect of molecular weights on preparing GRIN rods is also discussed.

### EXPERIMENTAL

#### Materials

Methyl methacrylate (MMA) (99%, Janssen), benzyl methacrylate (BzMA) (98%, TCI), benzoyl peroxide (BPO) (98%, Jia Hwa Chemical, Co.), and *n*-butyl mercaptan (*n*BM) (Janssen) were used without further purification. PMMA tubes which had a length of 28.7 cm and the outside and inside diameters of 15 and 11 mm, respectively, were purchased from Chi-Mai Co. The monomers MMA and BzMA have similar reactivity ratios and the refractive indices of their homopolymers were 1.49 and 1.56, respectively.

#### Preparation of GRIN Rods

The preparation of GRIN rods was basically performed by the method of Koike et al.<sup>2-8</sup> One end of the PMMA

\*  $r_1$  and  $r_2$  are the ratios of  $k_{11}$  over  $k_{12}$  and  $k_{22}$  over  $k_{21}$ , respectively, where  $k_{11}$ ,  $k_{12}$ ,  $k_{22}$ , and  $k_{21}$  are the rate constants of a propagating chain end in  $M_1$  adding to monomer  $M_1$ , a propagating chain ending in  $M_1$  adding to monomer  $M_2$ , a propagating chain ending in  $M_2$  adding to monomer  $M_2$ , and a propagating chain ending in  $M_2$  to monomer  $M_1$ .

**Table I The Formulations, Reaction Temperature ( $T$ ), and  $\Delta n$  of Samples a1–a3, b1–b5, and c1–c3**

Sample	BPO (wt %)	<i>n</i> BM (ppm)	$T$	$\Delta n$
a1	0.5	0	60	0.015
a2	0.75	0	60	0.014
a3	1.0	0	60	0.014
b1	0.5	0	60	0.015
b2	0.5	193	60	0.018
b3	0.5	386	60	0.018
b4	0.5	666	60	0.018
b5	0.5	1000	60	0.018
c1	1.0	0	57	0.015
c2	1.0	0	63	0.017
c3	1.0	0	70	— <sup>a</sup>

<sup>a</sup> The GRIN rod prepared at 70°C contained many bubbles and, hence,  $\Delta n$  was not measured.

tube was sealed with a silicon rubber stopper. The monomer mixture contained 20 mL of MMA and 5 mL of BzMA for each sample. Monomers, the initiator, and the chain-transfer agent were fed into the PMMA tube and mixed with an ultrasonic vibrator for 30 min. The mixture was then polymerized at a constant temperature for 8–16 h, followed by a postpolymerization at 90°C for 12 h under vacuum. The formulations and the reaction conditions are tabulated in Table I.

### Characterization

The refractive index profiles of the prepared GRIN rods were measured using a York P102 profile analyzer, in which a matching oil with a refractive index of 1.458 was used as the reference. The prepared GRIN rod with a 12 mm diameter was cut into four portions along the radial direction. The average molecular weight of each portion was measured by a gel permeation chromatography (GPC), which was calibrated with polystyrene standards and THF was used as the solvent at 40°C. The defect of bubbles was evaluated by counting the number of bubbles inside the GRIN rod while that of the mistiness was evaluated from an optical transmission test. The optical transmission test was equipped with a power supply (40 V, 25 A), a light source (24 V, 250 W), baffles, and an integral sphere. The transmission of the GRIN rod was determined by comparison with the blank condition.

## RESULTS AND DISCUSSION

### Effect of Initiator Concentration

The GRIN rods prepared from samples a1–a3 were transparent and also showed the decrease of the bubble defect

with increasing the initiator concentration from 0.5 to 1.0 wt %. These phenomena could be accounted for as follows: For a radical polymerization, increasing the initiator concentration would decrease the average molecular weight of the resulting polymer.<sup>9</sup> This was confirmed by the GPC results of samples a1–a3 in Table II. This table shows that the average molecular weights of samples a1, a2, and a3 were  $116.3 \times 10^4$ ,  $112.8 \times 10^4$ , and  $98.8 \times 10^4$ , respectively. The rapid polymerization of the reaction mixture resulted in a GRIN rod with a higher molecular weight, thereby leading to the shrinkage of the GRIN rod and bubbles were thus formed in the rod. Increasing the initiator concentration resulted in a decrease of molecular weight and led to a lower viscosity of the reaction mixture, which could fill the voids resulting from the shrinkage of the prepared GRIN rod. Therefore, the defect of bubbles in GRIN rods was reduced by increasing the initiator concentration used in the polymerization.

Figure 1 shows the refractive index distribution of the GRIN rod prepared from samples a1–a3. This figure revealed that the initiator concentration did not significantly affect both the profiles and  $\Delta n$ .

### Effect of Chain-transfer Agent

The GRIN rods prepared from samples b1–b5, which had different concentrations of the chain-transfer agent *n*BM, showed the decrease of the defects of bubbles and mistiness with increasing concentrations of *n*BM. Increasing the concentration of the chain-transfer agent inhibited the rapid growth of the polymer chain, therefore reducing the molecular weight of the prepared GRIN material. This prediction was confirmed by the average molecular weights of samples b1–b5 in Table II. The average molecular weight of samples b1–b5 decreased from  $122 \times 10^4$  to 22

**Table II The Molecular Weight of Each Layer<sup>a</sup> and Average Molecular Weight ( $\bar{M}_w$ ) of the GRIN Rods Prepared from Samples a1–a3 and b1–b5**

Sample	$M_w (\times 10^{-4})$				$\bar{M}_w$
	1st Layer	2nd Layer	3rd Layer	4th Layer	
a1	130	117	111	107	116.3
a2	132	124	92	103	112.8
a3	112	124	85	74	98.8
b1	124	138	120	106	122
b2	90	85	66	52	73.3
b3	77	74	49	47	61.8
b4	76	49	29	30	46
b5	28	25	17	18	22

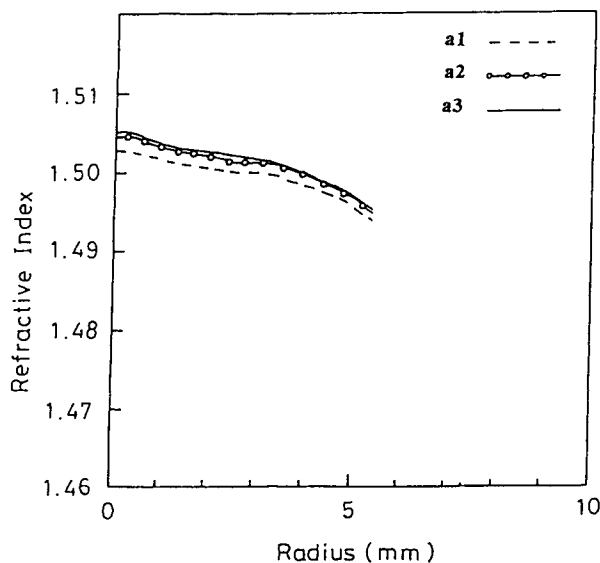
<sup>a</sup> The layer number of each sample was counted from the periphery of GRIN rod as the 1st layer to the center of the GRIN rod as the 4th layer.

$\times 10^4$  when the concentration of *n*BM increased from 0 to 1000 ppm. Hence, the viscosity of the reaction mixture and the shrinkage of the polymers were largely reduced with increasing the concentration of *n*BM. Therefore, the defect of bubbles in GRIN rods was decreased. The mistiness of the prepared GRIN rods, which resulted from phase separation due to the homopolymerization of MMA or BzMA, was also reduced with increasing the concentration of *n*BM.

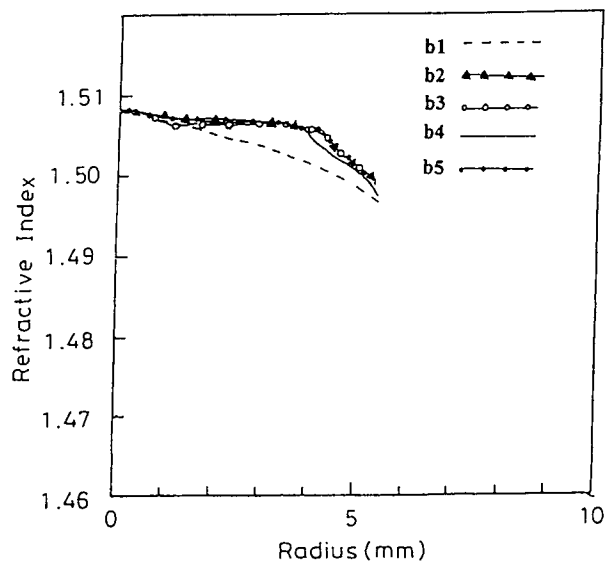
Figure 2 shows the refractive index profiles of the GRIN rods prepared from samples b1–b5. Although the  $\Delta n$  values were almost the same with increasing the amounts of *n*BM added, the profiles of the GRIN rods of samples b2–b5 were quite different from that of sample b1. There was no variation of refractive indices in the 0–4 mm region from the center of the GRIN rods for samples b2–b5. The formation of the gradient index in GRIN rods was obtained by the gel effect in the monomer system of MMA and BzMA. Hence, the present result suggests that the addition of the chain-transfer agent led to a polymer with a low molecular weight and an insignificant gel effect.

#### Effect of Reaction Temperature

The effect of temperature can be observed from the GRIN rods prepared from samples a1 and c1–c3, which had the reaction temperatures of 60, 57, 63, and 70°C, respectively. The polymerization rate increased with increasing the reaction temperature, subsequently resulting in a faster rate of shrinkage at a higher temperature. Hence, the defect of bubbles increased after a critical temperature. The experimental result revealed that the GRIN rod prepared at 70°C contained many bubbles, which could have a severe



**Figure 1** The refractive index profile of the GRIN rods prepared from samples a1–a3, as measured from the center of the rod to the periphery.



**Figure 2** The refractive index profile of the GRIN rods prepared from samples b1–b5, as measured from the center of the rod to the periphery.

effect on the transmission of data and image transfer of the rod. A comparison of the results at 57, 60, and 63°C suggested that the reaction temperature did not show a significant effect on both the value of  $\Delta n$  and the profile of the refractive index distribution. This might be because the temperature range investigated was not sufficiently large. A further investigation of a wide temperature range would be required to elucidate the temperature factor on preparing the GRIN rod.

#### CONCLUSIONS

The effects of reaction conditions on the formation of defects and the refractive index profile of the GRIN rods were investigated. Increasing the concentration of initiator, BPO, from 0.5 to 1.0 wt %, and the chain-transfer agent, *n*BM, from 0 to 1000 ppm, reduced the defect of bubbles because of reducing the shrinkage of the GRIN polymers from decreasing the molecular weights of the prepared polymers. The mistiness of the prepared GRIN rods was reduced with increasing the amounts of the added *n*BM. The defect associated with bubbles increased at a higher temperature of 70°C due to the higher polymerization rate, thereby leading to a rapid shrinkage of the prepared polymers. The value of  $\Delta n$  was not significantly affected by changing the concentrations of BPO, *n*BM, and the reaction temperature. However, *n*BM affected the refractive index profile in the GRIN rods due to the insignificant effect of the gel effect.

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## REFERENCES

1. Y. Koike, in *Polymers for Lightwave and Integrated Optics*, L. A. Hornak, Ed., Marcel Dekker, New York, 1992, p. 71.
2. Y. Koike, T. Ishigure, A. Horibe, and E. Nihei, in *Second International Conference on Plastic Optical Fibers and Applications*, The Hauge, June 28–29, 1993, p. 54.
3. Y. Koike, Y. Hondo, and E. Nihei, *SPIE*, **1592**, 62 (1991).
4. Y. Koike, Y. Takezawa, and Y. Ohtsuka, *Appl. Opt.*, **27**, 486 (1988).
5. Y. Koike, N. Tanio, F. Nihei, and Y. Ohtsuka, *Polym. Eng. Sci.*, **29**, 1200 (1989).
6. Y. Koike, E. Nihei, N. Tanio, and Y. Ohtsuka, *Appl. Opt.*, **29**, 2686 (1990).
7. Y. Ohtsuka, E. Nihei, and Y. Koike, *Appl. Phys. Lett.*, **57**, 120 (1990).
8. Y. Koike, *Polymer*, **32**, 1737 (1991).
9. G. Odian, *Principles of Polymerization*, Wiley, New York, 1991, Chap. 3.
10. S. Y. Yang, B. C. Ho, Y. H. Chang, J. J. Chen, T. W. Tseng, and M. S. Lee, *SPIE*, **2000**, 396 (1993).

S. Y. YANG  
Y. H. CHANG  
B. C. HO  
W. C. CHEN\*  
T. W. TSENG

Union Chemical Laboratories  
Industrial Technology Research Institute  
Hsinchu, Taiwan 300  
Republic of China

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\* To whom correspondence should be addressed.