Polymer Vol. 39 No. 22, pp. 5549–5552, 1998

0032-3861/98/$ - see front matter
PII: S0032-3861(97)10193-8

Preparation and characterization of gradient refractive index polymer optical rods

Jui-Hsiang Liu*, Hung-Tsai Liu and Yi-Bin Cheng
Department of Chemical Engineering, National Cheng Kung University, Tainan, 70101 Taiwan, ROC
(Revised 6 October 1997)

Gradient refractive index (GRIN) polymer optical rods were fabricated by the swollen-gel polymerization technique. The mechanism and preparation conditions of the swollen-gel polymerization were investigated. The effects of initiator concentration, swelling temperature, polymerization temperature and monomer feed ratios on the optical properties of the GRIN polymer rods were studied. To reduce the swelling time, two different kinds of initiator were compared. The gradient refractive index profiles of the plastic rods were estimated. The image observed through the GRIN polymer rod was also examined. © 1998 Elsevier Science Ltd. All rights reserved.

(Keywords: optical rod; gradient refractive index rod; swollen-gel polymerization)

INTRODUCTION

Gradient refractive index (GRIN) optical polymers have recently attracted extensive interest because of their potential application in optical communications[1] and image-transfer systems[2]. Polymer materials have certain advantages over glass in some cases, such as light weight, large numerical aperture (*NA*), flexibility and low processing cost. The so-called GRIN rods are made in the form of a cylinder several millimetres in diameter in which the refractive index decreases smoothly from the central axis towards the periphery of the rod. The refractive index profile obeys the following equation[3,4]:

$$n(r) = n_0\left(1 - Ar^2/2R_p^2\right) \quad (1)$$

where $n(r)$ is the refractive index at any distance r, n_0 is the refractive index on the optical axis, A is the quadratic gradient constant, r is radial distance from the optical axis, and R_p is the radius of the rod.

Furthermore, the optical properties of the GRIN rod are given by:

$$NA = \left(n_0^2 - n_p^2\right)^{0.5} = \left(2n_0\Delta n\right)^{0.5} = n_0\left(R_c/R_p\right)A^{0.5} \quad (2)$$

$$\Delta n = n_0 - n_p \quad (3)$$

where the NA value is the numerical aperature, which is related to acceptable optical angle, n_p is the refractive index of the periphery of the rod and R_c is the quadratic index distribution region.

Several methods have been reported for preparing GRIN polymer rods[5–12]. Gradient refractive index distribution inside the rod fabricated by the methods mentioned above is achieved mainly by use of the molar ratio, reactivity and diffusion rate of the component monomers. In our previous short communication[13], we reported a new preparation process called 'swollen-gel polymerization'. In this paper, the effects of initiator concentration, swelling temperature, polymerization temperature and the monomer feed ratio on the optical properties of GRIN polymer rods were studied. The image observed through the GRIN polymer rod was also examined.

* To whom correspondence should be addressed

EXPERIMENTAL

Materials

Methyl methacrylate (MMA) (99%, from TCI) was used as the monomer (M_1) having a lower refractive index, the refractive index of poly(methy methacrylate) (PMMA) being 1.49. Benzyl methacrylate (BzMA) (99%, from TCI) was used as the monomer (M_2) with higher refractive index; the refractive index of poly(benzyl methacrylate) (PBzMA) is 1.57. Here, benzoyl peroxide (BPO) and dicumyl peroxide (DCPO) were used as thermal initiators. The number-average molecular weight of the PMMA used in this investigation is about 1×10^6.

Preparation of GRIN plastic optical rods

In the swollen-gel polymerization, a mixture of MMA and BzMA monomers with a specified amount of thermal initiator, BPO or DCPO, was poured into a PMMA tube. The outer and inner diameters of the tube were 15 mm and 9 mm, respectively. The tube containing the monomer mixture was then heated at a lower temperature, T_1, for t hours. During the initial stage, the monomer mixture was absorbed into the inner surface of the plastic tube and a gel phase (swollen gel) was formed between the monomer solution and the polymer wall. Since the solubility parameter of the monomer mixture used in this investigation is near that of the polymer, the polymer wall can easily be swollen by the monomer solution. As monomer mixture continuously penetrated into the plastic wall during the swelling period, the swollen gel was getting thicker and the polymer wall was getting thinner.

After completion of the swelling process at the lower temperature T_1, the monomer distribution in the gel rod was then fixed by a futher polymerization of the monomer mixture at a higher temperature, T_2. The refractive index profile of the prepared GRIN rod was measured with a York-P102 profile analyser. The refractive index of the matching oil used in the system is 1.458. The image through the GRIN polymer rod of a chequered pattern with 6 mm squares was also examined.

RESULTS AND DISCUSSION

Formation of GRIN profile

During the swelling process, a swollen gel was formed by penetration of the monomer mixture into the polymer wall. It was found that polymerization of the monomer solution hardly takes place during the swelling period because of the presence of an inhibitor (200 ppm hydroquinone) in the monomer mixture. Use of a high-molecular-weight PMMA tube ($M_w = 1\times10^6$) leads to the swollen-gel structure being maintained during the swelling stage. The density of the swollen gel decreased and the content of BzMA increased from the periphery to the central axis of the rod. The results suggest that the GRIN profile of the rods is formed mainly by the distribution of the BzMA component.

Preparation of bubble-free rods

The monomer mixture and initiators were fully diluted by the swollen gel during the swelling process, the gel was changed into a rubber-like state and had less shrinkage than in the liquid monomer solution. Hence, a bubble-free GRIN polymer optical rod was obtained. During the initial polymerization process, the diameter of the gel rod was expanded from 15 mm to 15.75 mm because of thermal expansion. We believe that the polymerization shrinkage was decreased mostly by the monomer distribution in the swollen gel, and the elasticity of the rod made it contract uniformly[14]. When the polymerization was completed, a slight shrinkage (about 3%) was found in the radial direction, and the diameter was changed from 15 mm (PMMA tube) to 14.5 mm (GRIN rod). The formation of a swollen gel means dispersion of the monomer mixture in the polymer matrix, which will also decrease the polymerization shrinkage.

Effect of initiator concentration on the optical properties of the rods

The optical characteristics of GRIN rods prepared with various initiator concentrations are listed in *Table 1*. Benzoyl peroxide (BPO) was used as initiator, MMA/BzMA = 4/1, $t = 33$ h, $T_1 = 43$°C and $T_2 = 80$°C. As can be seen in *Table 1*, the values of Δn, *NA* and *A* evidently increase with increasing concentration of BPO, but R_c/R_p remains steady at about 80%. When BPO = 0.2 wt%, some bubbles were found in the rods, and when the initiator content was above 0.2 wt%, all rods were full of bubbles. The refractive index distribution profiles of the rods thus prepared are shown in *Figure 1*; the profiles are almost quadratic from the centre axis to the periphery of the rod.

Table 1 Effect of initiator concentration on the optical characteristics of GRIN rods[a]

	BPO (wt%)		
	0.1	0.15	0.2[b]
Δn	0.0143	0.0145	0.0149
NA	0.2066	0.2084	0.2111
A	0.01377	0.01378	0.01481
R_c/R_p (%)	79	81	80

[a]BPO was used, $t = 33$ h, $T_1 = 43$°C, $T_2 = 80$°C, MMA/BzMA = 4/1
[b]Some bubbles were found

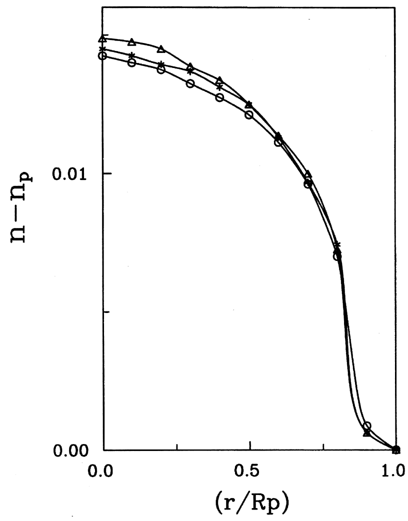

Figure 1 Refractive index profiles of GRIN rods prepared with various BPO concentrations (wt%): ○, 0.1; ∗, 0.15; △, 0.2

Effect of swelling time on the optical characteristics of the rods

Optical characteristics of GRIN rods prepared at different swelling times are listed in *Table 2*. The conditions were 0.15 wt% BPO, MMA/BzMA = 4/1, $T_1 = 43$°C and $T_2 =$ 80°C. *Table 2* shows that Δn and *NA* values decrease with increasing swelling time, and R_c/R_p is constant at about 80%. When the swelling time is less than 30 h, many bubbles formed after completion of the polymerization. In contrast, deformation of the cylindrical shape occurred when the swelling time was longer than 39 h. It was found that some wrinkles formed on the outer surface of the rods at swelling time of 39 h. The refractive index profiles of the rods are shown in *Figure 2*, where quadratic profiles can also be observed.

Table 2 Effect of swelling time on the optical characteristics of GRIN rods[a]

	t (h)			
	30	33	36	39[b]
Δn	0.0149	0.0145	0.0143	0.0140
NA	0.2114	0.2084	0.2071	0.2047
A	0.01357	0.01378	0.01408	0.01394
R_c/R_p (%)	78	81	81	81

[a]BPO = 0.15 wt%, $T_1 = 43$°C, $T_2 = 80$°C, MMA/BzMA = 4/1
[b]Wrinkles formed on the outer surface of the rods

Effect of swelling temperature

Table 3 presents the optical characteristics of GRIN rods prepared at different swelling temperatures, where MMA/BzMA = 4/1, $t = 33$ h, $T_2 = 80$°C and BPO = 0.15 wt%. Δn, *NA* and *A* values in *Table 3* decrease with increasing swelling temperature, while R_c/R_p is still steady at about 80%. The results suggest that further diffusion at higher temperature will lower the Δn of the GRIN rods. Refractive index profiles for these rods are shown in *Figure 3*.

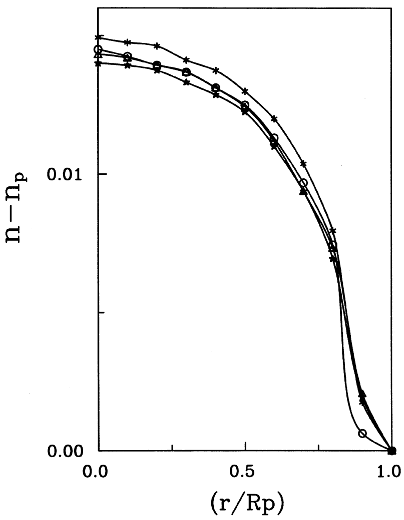

Figure 2 Effect of swelling time on the refractive index profiles of GRIN rods. t (h): ∗, 30; ○, 33; △, 36; ★, 39

Table 3 Effect of swelling temperature (T_1) on the optical characteristics of GRIN rods[a]

	T_1 (°C)		
	38	43	48
Δn	0.0153	0.0145	0.0131
NA	0.2141	0.2084	0.1976
A	0.01491	0.01378	0.01359
R_c/R_p (%)	79	81	81

[a]BPO = 0.15 wt%, t = 33 h, T_2 = 80°C, MMA/BzMA = 4/1

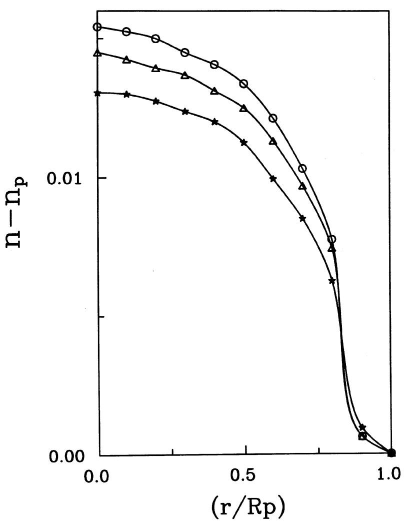

Figure 3 Swelling temperature dependence of the refractive index profiles of GRIN rods. T_1 (°C): ○, 38; △, 43; ★, 48

Table 4 Effect of polymerization temperature (T_2) on the optical characteristics of GRIN rods[a]

	T_2 (°C)			
	60	70	80	90[b]
Δn	0.0137	0.0140	0.0145	0.0146
NA	0.2029	0.2047	0.2084	0.2093
A	0.01669	0.01554	0.01378	0.01355
R_c/R_p (%)	77	83	81	81

[a]BPO = 0.15 wt%, T_1 = 43°C, MMA/BzMA = 4/1
[b]Wrinkles formed on the outer surface of the rods

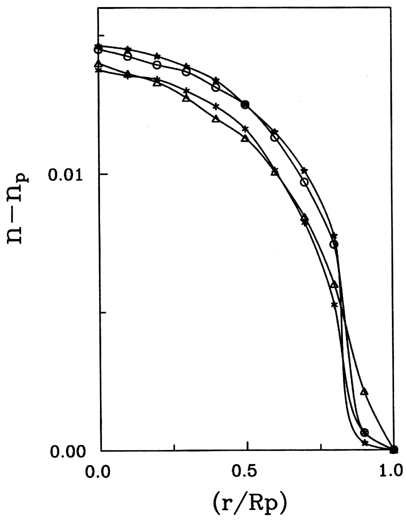

Figure 4 Polymerization temperature dependence of the refractive index profiles of GRIN rods. T_2 (°C): ∗, 60; ⩽, 70; ○, 80; ★, 90

Table 5 Half-lifes ($t_{1/2}$) of initiators[a]

	T (°C)[b]						
	50	70	85	100	115	130	145
BPO	84 h	7.3 h	1.4 h	19.8 min	—	—	—
DCPO	—	—	—	—	13 h	1.7 h	16.8 min

[a]Benzoyl peroxide (BPO) and dicumyl peroxide (DCPO) in benzene
[b]Reaction temperature

Effect of polymerization temperature

Table 4 shows the optical characteristics of GRIN rods prepared at various polymerization temperatures. The monomer composition was MMA/BzMA = 4/1, t = 33 h, T_1 = 43°C and BPO = 0.15 wt%. As shown in *Table 4*, Δn and *NA* values increase, but *A* decreases with increasing polymerization temperature. Wave-like wrinkles formed in the outer surface of the rods when the polymerization was carried out at 90°C. Deformation of the rods occurred when the polymerization temperature was higher than 100°C. As shown in *Figure 4*, symmetric quadratic refractive index profiles about the centre axis of the rod were again confirmed.

Effect of initiator type

It was found that the initiator plays an important role in the swelling process and polymerization stage of this swollen-gel polymerization method. During the swelling process, polymerization should be inhibited or avoided as much as possible. To reduce the swelling time, swelling at high temperature is necessary. Hence, a high-temperature initiator with a long half-life is needed. *Table 5* lists the half-lifes of the BPO and DCPO initiators. The half-life at any temperature can be estimated from[15]:

$$t_{1/2} = 0.693/k_d = \left(0.693/k_0\right)\exp\left(E_d/RT\right) \qquad (4)$$

where k_d is the dissociation rate constant of the initiator, k_0 is the frequency factor, E_d is the activation energy for dissociation of the initiator (J mol^{-1}), R is the gas constant (equal to 8.314 J g^{-1} mol^{-1} K^{-1}), and T is the absolute temperature.

Benzoyl peroxide and dicumyl peroxide were selected as initiators and the optical properties of GRIN rods thus prepared are listed in *Table 6*. Detailed preparation conditions are listed below the table. *Table 6* reveals that

Table 6 Effect of initiator on the optical characteristics of GRIN rods

Initiator	Δn	*NA*	*A*	R_c/R_p (%)
BPO[a]	0.0145	0.2084	0.01378	81
DCPO[b]	0.0146	0.2093	0.01714	82

[a]BPO = 0.15 wt%, $t = 33$ h, $T_1 = 43°C$, $T_2 = 80°C$, MMA/BzMA = 4/1
[b]DCPO = 0.15 wt%, $t = 18$ h, $T_1 = 65°C$, $T_2 = 95°C$, MMA/BzMA = 4/1

Table 7 Effect of feed molar ratio on the optical characteristics of GRIN rods[a]

	MMA/BzMA		
	3/1	4/1	5/1
Δn	0.0154	0.0145	0.0124
NA	0.2148	0.2084	0.1926

[a]BPO = 0.15 wt%, $t = 33$ h, $T_1 = 43°C$, $T_2 = 80°C$

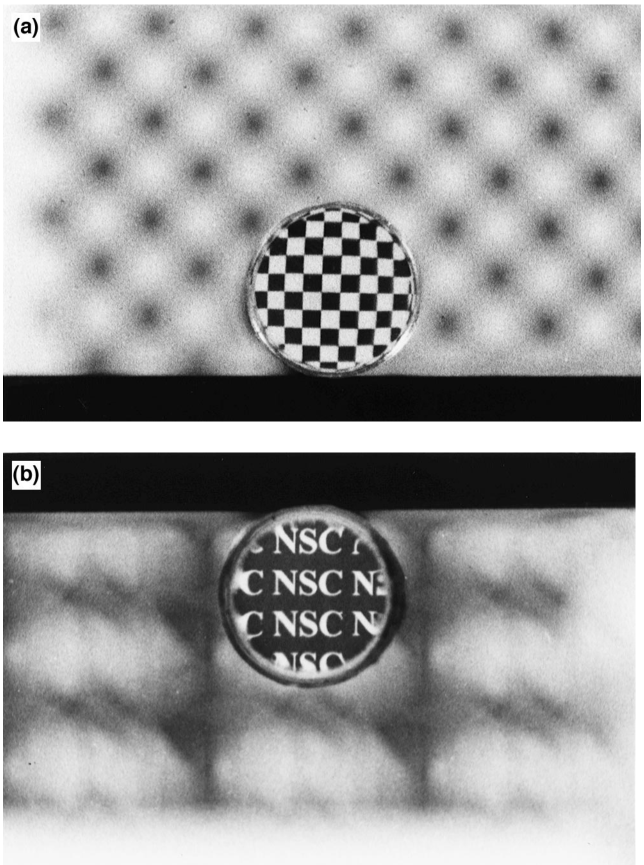

Figure 5 Image observed through the MMA/BzMAPAc = 4/1 (wt/wt) rod with 14.5 mm diameter and 150 mm length. (a) Real image of a 6 mm sqaure chequer pattern; distance between the object and the end of the rod is 200 mm. (b) Real image of the letters 'NSC' with 16 mm height and 40 mm width; distance between the object and the end of the rod is 280 mm

the optical characteristics of the different initiator systems are not so different. However, the swelling time of the DCPO system was reduced from 33 h to 18 h.

As shown in *Table 7*, Δn and *NA* values decrease with increasing MMA/BzMA ratio. Images of a chequered pattern with 6 mm squares and of the letters 'NSC' (16 mm high and 40 mm wide) observed through the GRIN rod are shown in *Figure 5a* and *b*. The diameter and length of the rod are 14.5 mm and 150 mm, respectively. As shown in the figures, no image distortion occurred through the GRIN rod prepared in this investigation.

CONCLUSION

In this investigation, bubble-free GRIN optical polymer rods with parabolic refractive index profiles were fabricated by the swollen-gel polymerization of a monomer mixture of MMA/BzMA. It was found that Δn and *NA* values increase with increasing initiator concentration, polymerization temperature (T_2) and monomer molar feed ratio. On the other hand, they decrease with increasing swelling time (t) and swelling temperature (T_1). The refractive index distribution constant (A) decreases with increasing swelling temperature (T_1) and polymerization temperature (T_2), but increases with increasing initiator concentration. The swelling period of the process can be reduced effectively by using DCPO, an initiator having a long half-life and high initiating temperature. Images with no distortion were observed through the GRIN rods fabricated by using the swollen-gel polymerization of a MMA/BzMA monomer mixture.

REFERENCES

1. Wilson, J. and Hawkes, J. F. B., *Optoelectronics: An Introduction*. Prentice-Hall, NJ, 1983, p. 357 and 377.
2. Koike, Y., Gradient index materials and components, In *Polymers for Lightwave and Integrated Optics*, ed. L. A. Hormak. Marcel Dekker, Inc., New York, 1992.
3. Kapron, F. P., *J. Opt. Soc. Am.*, 1970, **60**, 1433.
4. Rawson, E. G., Herriott, D. R. and McKenna, J., *Appl. Opt.*, 1970, **9**, 753.
5. Ohtsuka, Y. and Terao, Y., *J. Appl. Polym. Sci.*, 1981, **26**, 2907.
6. Ohtsuka, Y. and Sugaho, T., *Appl. Opt.*, 1983, **22**, 413.
7. Liu, J. H. and Chu, M. H., *Angew. Makromol. Chem.*, 1989, **174**, 1.
8. Koike, Y., Kimoto, Y. and Ohtsuka, Y., *Appl. Opt.*, 1982, **21**, 1057.
9. Koike, Y., Hidaka, H. and Ohtsuka, Y., *Appl. Opt.*, 1985, **24**, 4321.
10. Koike, Y. and Shimo, O., European Patent No. 496893A1 (1992).
11. Koike, Y., Takezawa, Y. and Ohtsuka, Y., *Appl. Opt.*, 1988, **27**, 486.
12. Koike, Y., US Patent No. 5 541 247 (1996).
13. Liu, J. H. and Liu, H. T., *Polymer*, 1997, **38**, 1251.
14. Sarti, G. C., Gostoli, C., Riccioli, G. and Carbonell, G., *J. Appl. Polym. Sci.*, 1986, **32**, 3627.
15. Odian, G., *Principles of Polymerization*, John Wiley & sons, ISBN 0471-00772-2.