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Preparation of gradient refractive index rod by swollen-gel polymerization

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A new method for preparing GRIN (gradient refractive index) polymer rod by using the swollen-gel polymerization technique was fabricated. Monomer pair systems of MMA (methyl methacrylate) with reactive BzMA (benzyl methacrylate) and unreactive BN (bromonaphthalene) and BPAc (benzyl phenyl acetate) were investigated. Two-dimensional refractive index profile of rods were estimated. A high NA (numerical aperture) value of 0.336 in system of MMA/BN = 2/1 was obtained. A good symmetric GRIN rod can be fabricated by using the swollen-gel polymerization. The image with no distortion can be observed through the GRIN rods fabricated by using the swollen-gel polymerization method. © 1997 Elsevier Science Ltd. All rights reserved.

(Keywords: gradient refractive index; swollen-gel; rod lens; gradient constant; numerical aperture)

Introduction

The GRIN (gradient refractive index) rod lens is a cylindrical medium with a parabolic refractive index distribution that is highest on its optical axis and decreases toward the periphery as the square of the radial distance from the optical axis. The refractive index at any distance r from the optical axis is given by the equation[1,2]

$$n(r) = n_0\left(1 - \frac{1}{2}Ar^2\right) \quad (1)$$

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, and r is the radial distance from the optical axis.

Owing to the GRIN distribution in the rod, it has imaging and light focusing properties, and can be used in copy machine, facsimile lens arrays and image transmission system[3], etc. GRIN polymer optical fibres with a large bandwidth of 2 GHz · Km and a low optical loss of 56 dB Km^{-1} at 688 nm were fabricated[4], and can be used in a communication system[5].

Transparent polymers used as GRIN materials have the advantages of excellent mechanical properties, good flexibility, easy processibility and low cost over quartz glass. Hence, the development of GRIN polymer has grown rapidly in recent years. Several methods have been used to prepare GRIN polymer optical devices, namely, two-step copolymerization[6–9], photopolymerization[10,11], chemical copolymerization[12], suspension polymerization[13], and interfacial-gel copolymerization[14].

As those described in the literature[14], copolymerization took place in the interfacial-gel phase is more fast than in the monomer mixture solution, thereby, GRIN copolymer is gradually formed in the direction from the periphery to the centre of the rod. Although GRIN rod can be prepared monolithically by the interfacial-gel polymerization, however, in our study and Yang's reports[15], it is found that the method is easy to form voids and bubbles resulting from the volume contraction of the GRIN polymer rod. During the copolymerization, monomers solution is not refilled into the polymer tube. So, a void space caused by the serious shrinkage sometimes tunnel through the polymer rod.

In connection with the studies on the preparation of GRIN rod fabricated in our previous paper[16], we reported a new method for preparing GRIN rod by using the swollen-gel polymerization technique fabricated in this investigation. In the technique, a GRIN profile can be formed by the swollen-gel extending from the peripheral wall of the original plastic tube, and the GRIN rod with no voids and bubbles can be fabricated easily by this technique. Effects of reaction temperature, molar ratio of composition, and swelling conditions on the formation of GRIN profile and Δn of the rods were studied, the image transmission of the GRIN rods were also investigated.

Experimental

Materials. Methyl methacrylate (MMA) (99%, from TCI) was used as a lower refractive index monomer M_1 and M_2, with a higher refractive index, here, we used two different systems: one is the reactive benzyl methacrylate (BzMA, 98% from TCI), and the other is the unreactive agent chosen from bromonaphthalene (BN, 98% from Ferak) and benzyl phenyl acetate (BPAc, 99% from TCI). Benzoyl peroxide (BPO) was used as the initiator. To prevent the occurring of polymerization during the swelling period, all commercial materials were used without any further purification. Reagent ratio used in this investigation are all weight percentage. The refractive index of MMA, BzMA, BN and BPAc are 1.490, 1.586, 1.660 and 1.555, respectively.

Preparation of GRIN polymer rod. *Figure 1* shows the diagram of the preparation procedure for the GRIN rod

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fabricated in this investigation. The monomer mixture (M_1, M_2 and initiator) was poured into a PMMA tube. The inner and outer diameters of the tube are 10 and 15 mm, respectively. The tube with monomer mixture was then heated at a lower temperature T_1 for t_1 hours. During the initial stage, the monomer mixture was absorbed into the inner surface of the plastic tube, and a gel phase front was formed between the monomer solution and the polymer wall.

Since the solubility parameter of monomer mixture used in this investigation is near that of polymer, the polymer tube can be easily swollen by the monomer solution. Monomer solution continuously penetrated into the polymer wall during the swelling period, the swollen-gel was getting thicker and the polymer wall was getting thinner. Finally, all the mixture in the tube was changed into a gel state completely.

After completion of the swelling process at the lower temperature T_1, the monomer distribution was then fixed by a further polymerization of monomer mixture at

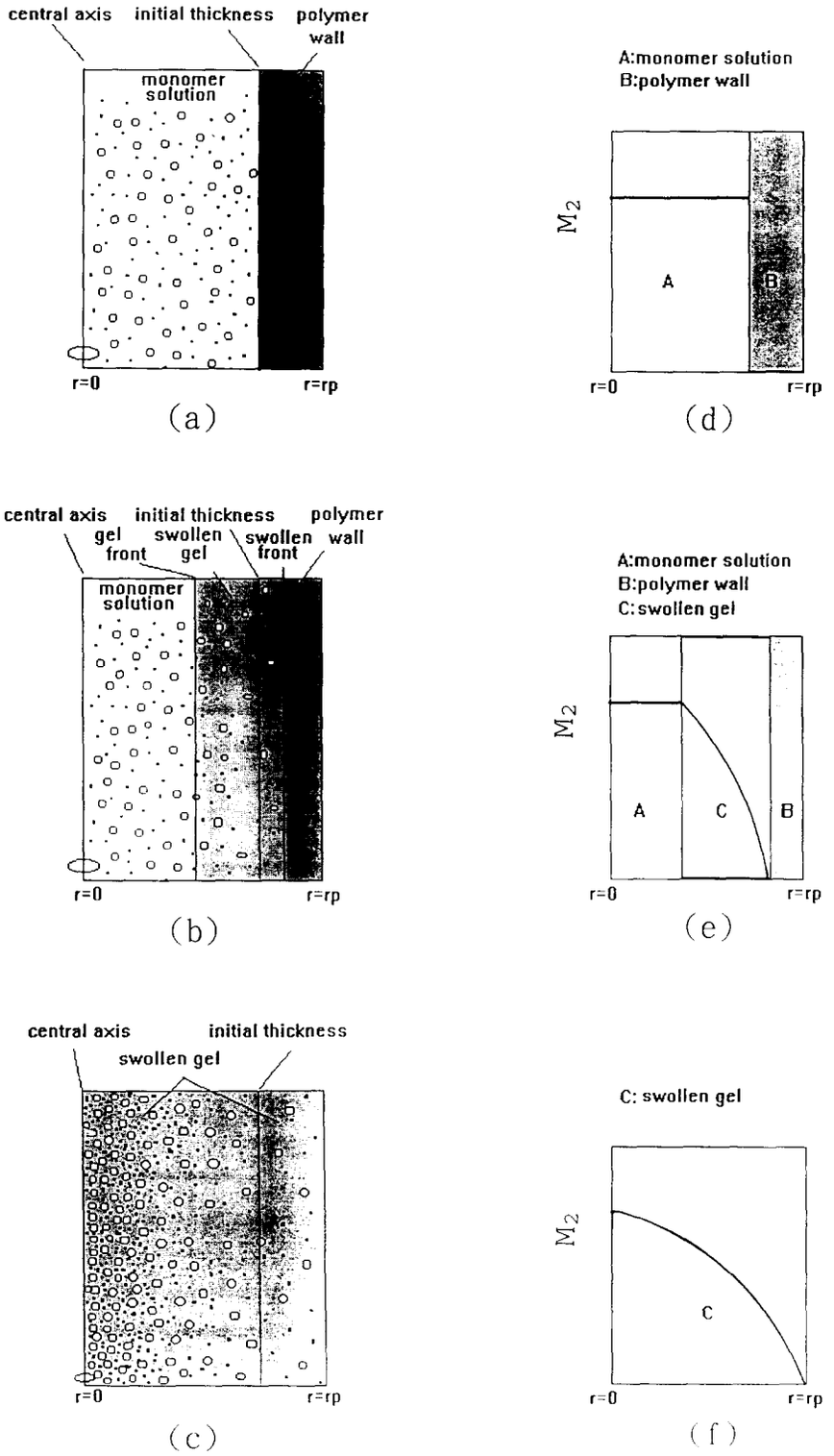

Figure 1 (a)–(c) Preparation procedure of GRIN rod using swollen-gel polymerization. (●) M_1, (○) M_2

a higher temperature T_2. The monomer mixture and initiator were fully diluted by the swollen gel during the swelling process, the gel was changed into a rubber state[17] and has a less shrinkage than in the liquid monomer solution. Hence, a bubble-free GRIN polymer optical rod was obtained. The refractive index profile of the prepared GRIN rod was measured using a York P102 profile analyser. The refractive index of the matching oil used in the system is 1.458.

Results and discussion

Optical characteristics of GRIN rods prepared by the swollen-gel polymerization with various materials and molar ratios are listed in *Table 1*. Δn is the refractive index difference between the centre and the periphery of the rod, NA is numerical aperture and θ_{max} is the maximum acceptance angle; both of them can be calculated from

$$NA = \sin\theta_{max} = (2\Delta n \cdot n_0)^{0.5} \quad (2)$$

Here n_0 is the refractive index at the centre of the rod.

In *Table 1*, we can see that all the Δn, NA and θ_{max} increased with increasing the amount of M_2 agent, and MMA/BN system has a higher refractive difference (Δn) owing to the higher refractive index of BN ($n = 1.660$). The highest NA value of 0.336 was obtained in a system of MMA/BN = 2/1. As we know, high NA value or high acceptable angle (θ_{max}) will bring about a high brightness, and the high brightness is a necessary factor for the GRIN lens to achieve high-speed scanning or make the machine compact when using GRIN rods in an image-transmission system.

Figure 2 shows GRIN profiles of the rods prepared in swollen-gel polymerization method using MMA/BN, MMA/BPAc, and MMA/BzMA material pairs in the ratio of 4/1. As can be seen in *Figure 2*, Δn of MMA/BN, MMA/BPAc and MMA/BzMA rods decrease in order. The refractive index profiles are almost quadratic from the centre axis to the periphery.

Figure 3 shows the three-dimensional refractive index profile of a GRIN rod. The result suggests that a good symmetric GRIN rod can be fabricated by using the swollen-gel polymerization.

Table 1 Optical characteristics of GRIN rods[a]

Agent	MMA/Agent	No.[b]	Δn	NA	$2\theta_{max}$
BN	4/1	a	0.023	0.264	30.6
	3/1		0.028	0.291	33.9
	2/1		0.037	0.336	39.2
BPAc	4/1	b	0.018	0.235	27.2
	3/1		0.022	0.258	29.9
	2/1		0.026	0.281	32.6
BzMA	5/1	c	0.012	0.190	21.9
	4/1		0.014	0.201	23.5
	3/1		0.015	0.213	24.6

[a] Swollen at 40°C for 30 h and then heated at 80°C for 24 h
[b] Curve number in *Figure 2*

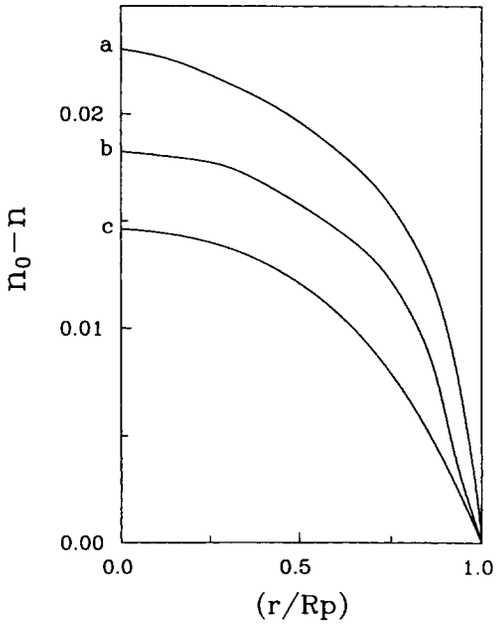

Figure 2 Refractive index profiles of GRIN rods (MMA/M_2 = 4/1). M_2 in curves *a*, *b* and *c* are BN, BPAc and BzMA, respectively

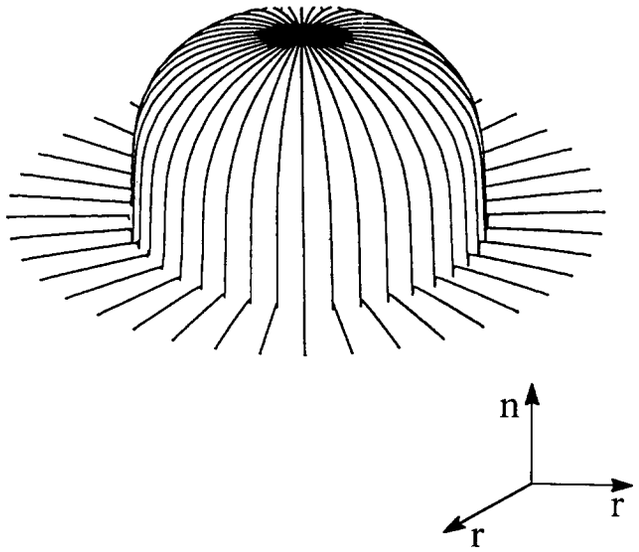

Figure 3 3-D refractive index profile of GRIN rod (MMA/BPAc = 4/1)

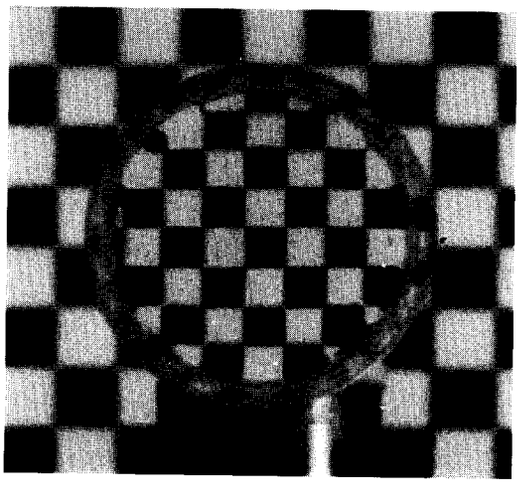

Figure 4 Image observed through the MMA/BPAc = 4/1 rod with 14.5 mm diameter and 110 mm length. Real image of a checker pattern with 7 × 7 mm^2, the distance between the object and the end face of rod is 125 mm

Figure 4 shows the real image of a checkered pattern with 7 mm square through the GRIN rod prepared in MMA and unreactive agent system (MMA/BPAc = 4/1). Here the diameter and the length of the rod are 14.5 mm and 110 mm, respectively. The distance between the checkered pattern and the end face of the GRIN rod is 125 mm.

As shown in *Figure 4*, no image distortion was considered. The results suggest that a GRIN plastic optical rod can be fabricated by using the swollen polymerization method.

Conclusion

A novel method for preparing a GRIN polymer rod by using the swollen-gel polymerization technique was fabricated. Systems of MMA with those reactive and unreactive agents were investigated. It was found that Δn and NA values of MMA with unreactive agent are larger than those of reactive agent system, and a high NA value of 0.336 in MMA/BN = 2/1 was obtained. The image with no distortion can be observed through the GRIN rods fabricated by using the swollen-gel polymerization method.

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