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The Large Dimensional Radial GRIN Polymer

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ABSTRACT: A new method for preparing very large radial-GRIN (graded index) polymer plates is proposed. The resulting radial-GRIN plate has a diameter of 70 mm of the GRIN region and Δn of 0.02. The optical characteristics of the large radial-GRIN lens were estimated by calculating the trajectory of a ray through GRIN lens which was based on Maxwell's ray equation. It was confirmed that such large GRIN polymers are promising for eye glasses with no spherical aberration or multifocus properties.

KEY WORDS Copolymerization / GRIN / Lens / Large Dimensional / Radial GRIN Polymer / Maxwell's Ray Equation / Methyl Methacrylate / Spherical Aberration / Mold /

Recently, optical technology has progressed with various organic and inorganic materials. The GRIN (graded index) optical materials are expected as rod lens, low spherical aberration lens, and high bandwidth optical fibers,[1-6] etc. For example, the GRIN lens array which is made by arranging hundreds of GRIN rod lenses has been used for small copy-machines.[7]

Most GRIN materials have been made by inorganic materials. On the other hand, it has been reported that GRIN material can be synthesized by organic materials more mildly than inorganic materials.[8] Regardless of organic or inorganic materials, GRIN materials so far have only small size in diameter as $\phi \fallingdotseq 10$ mm, which is too small to be used for eyeglasses or camera lenses.

In this paper, we propose a new technique, a curved mold method, for preparing the very large radial-GRIN polymer plate that has the diameter of 70 mm. Conventional diffusion process of forming the radial-GRIN polymer has been based on monomer diffusion from the periphery to the center. Therefore, the dimensions of the GRIN region are restricted by the possible diffusion distance of monomer. On the other hand, the curved mold method provides the radial-GRIN polymer by monomer diffusion in the thickness direction (not in the radial direction). Therefore, very large radial GRIN polymer can be easily prepared by this method.

Further, the optical characteristics of the large radial-GRIN lens was estimated by calculating the trajectory of a ray through GRIN lens which was based on Maxwell's ray equation. It was confirmed that such large GRIN polymers are promising for eye glasses with no spherical aberration or multifocus properties, maintaining single spherical curvature of lens.

PREPARATION OF LARGE RADIAL-GRIN PLATE

Materials

Methyl methacrylate (MMA) distilled at 46°C/100 mmHg was used as the M_1 monomer. Styrene (St) distilled at 42°C/25 mmHg was used as the M_2 monomer. The refractive indices of poly(MMA) and poly(St) are 1.492 and 1.592, respectively. Ethylene glycol dimethacrylate (EDMA) distilled at 56°C/0.02 mmHg was used as a crosslinking reagent. Benzoyl peroxide (BPO) recrystallized from chloroform-cold methanol was used as an initiator and *n*-Butyl mercaptan (nBM) was used as a chain transfer reagent without any purification.

Preparation Method of Large GRIN Lens

A large GRIN lens with a continuously changed refractive index profile from the center axis to the periphery was prepared by a new copolymerization technique that is the curved mold method. A schematic representation of this method is shown in Figure 1, which is divided into 3 steps. First, the M_1 monomer was partially polymerized at 70°C for 30 min to obtain sol state. Then the M_1 sol having the monomer conversion of 5 wt% was poured into the curved-shape glass mold as shown in Figure 1 (first step), then the curved-shape preform gel (or polymer) was formed by heating at 60°C for one hour. Secondly, the curved mold (upper side in the first step) was removed and another curvature mold was assembled on the upper side (In Figure 1 (second step), a flat plate is shown as an upper side mold). Thereafter, the M_2 monomer was filled in the gap between the preformed M_1 gel and upper side mold (Figure 1 (second step)). Thirdly, by heating at 70°C for one day, the preformed M_1 gel and M_2 monomer were gradually copolymerized. During the third step, at the interface between preformed M_1 gel and M_2 monomer, the preformed M_1 gel is well dissolved in M_2 monomer and gradually diffuses into M_2 monomer phase. Therefore, this initial interface gradually disappears and mutual diffusion between M_2 monomer and M_1 gel is performed in the direction normal to the interface between M_1 gel and M_2 monomer phases. The thickness of t in Figure 1 is much shorter than the radius R_p of plate and the ratio of M_1 to M_2 gradually increases with the distance r from the center of the plate. Therefore, after enough mutual diffusion between M_1 and M_2, the composition of M_1 and M_2 in the direction of thickness becomes almost homogenized because of thin thickness t however, the ratio of M_1 to M_2 at the distance r still keeps the gradient in the radial direction of r because of very large R_p compared to t. Since the refractive indices of M_1 and M_2 polymers are different from each other, some radial refractive index profile is formed (see Figure 1 (third step)). In the conventional diffusion process, M_2 monomer is diffused from the periphery of M_1 polymer or gel preform to the center region. Therefore, the direction of M_2 monomer diffusion and the direction of the refractive index distribution are the same. So, when the diameter of M_1 preform rod is larger than 10 mm, it is difficult to achieve a desired refractive index profile in the radial direction. However, in this method, the diffusion of M_2 monomer is virtually in the normal direction (not radial direction) and the dimension of this diffusion is of several millimeters. Therefore, in this method, there is no limitation for obtaining the very large

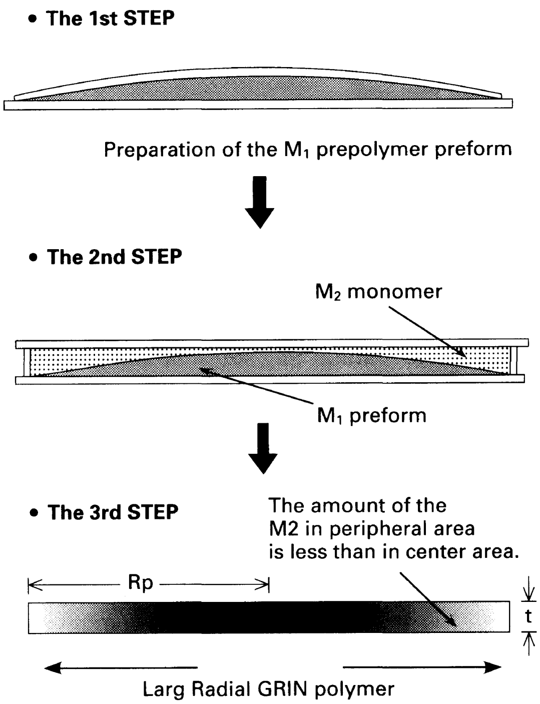

Figure 1. Curved mold method for preparing the large GRIN polymer plate.

dimension of R_p in principle.

OPTICAL PROPERTIES OF RADIAL-GRIN POLYMER

The refractive index distribution along the radial direction was measured by the partial splitting method using Interphako[9] interference microscopy. The representative refractive-index distribution of the GRIN polymer is shown in Figure 2. The preparation of this sample was carried out under the conditions mentioned above. The curvature radius R_1 of the curved-shape mold of the upper side in Figure 1 (first step) was 200 mm and the thickness t was 2 mm. The index distribution region of the plate was 70 mm which was much larger than any existent GRIN materials so far.

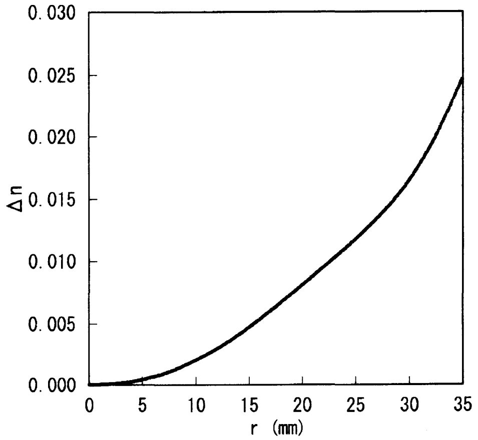

Figure 2. Refractive index distribution of the large GRIN polymer.

As shown in Figure 2, the refractive index distribution was similar to the quadratic distribution. In this method, the M_1 preform gel can be formed by many molds with different curvatures. Additionally, there are many monomer combinations of M_1 and M_2. Therefore, this new method can provide many index-profiles and Δn.

Figure 3 shows a photograph of the image formed through the radial GRIN polymer plate shown in Figure 2. The distance between the object (stripe pattern) and the radial GRIN plate was 2 m. The sample was quite transparent for this thickness of plate.

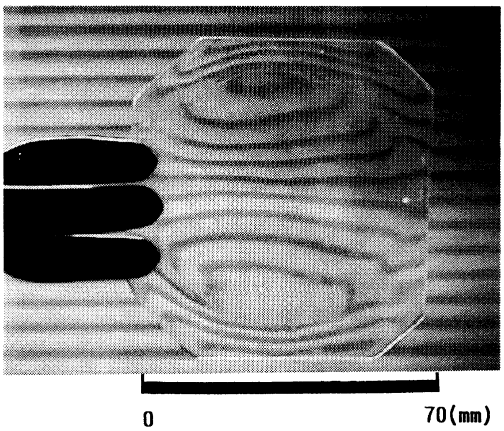

Figure 3. Photograph of image formed through the GRIN polymer plate with a 2 mm thickness.

RAY TRACING THROUGH RADIAL GRIN LENS

A ray tracing program to calculate the trajectory of a ray through the large radial GRIN polymer lens was made. In general, the ray trajectory through a heterogeneous medium, where the refractive index was a function of the position, satisfies Maxwell's ray equation 1:

$$\frac{\mathrm{d}}{\mathrm{d}s}\left(n(r)\frac{\mathrm{d}r}{\mathrm{d}s}\right)=\nabla n(r) \tag{1}$$

where ds is differential element of path length along the ray, $n(r)$ is the refractive index distribution, and r is the position vector of a point on the ray. When a variable t is introduced as written in eq 2, the eq 1 is converted to eq 3.[10]

$$t=\int\frac{\mathrm{d}s}{n} \tag{2}$$

$$\frac{\mathrm{d}^2r}{\mathrm{d}t^2}=n\nabla n \tag{3}$$

Equation 3 can be written as the matrix equation eq 4, defining following three components as eq 5.

$$\frac{\mathrm{d}^2 P}{\mathrm{d}t^2} = D(P) \tag{4}$$

$$P \equiv \begin{pmatrix} x \\ y \\ z \end{pmatrix}; \quad T \equiv \begin{pmatrix} T_x \\ T_y \\ T_z \end{pmatrix} \equiv \begin{pmatrix} \mathrm{d}x/\mathrm{d}s \\ \mathrm{d}y/\mathrm{d}s \\ \mathrm{d}z/\mathrm{d}s \end{pmatrix};$$

$$D \equiv n \begin{pmatrix} \partial n/\partial x \\ \partial n/\partial y \\ \partial n/\partial z \end{pmatrix} \equiv 1/2 \begin{pmatrix} \partial n^2/\partial x \\ \partial n^2/\partial y \\ \partial n^2/\partial z \end{pmatrix} \tag{5}$$

Equation 4 is to be solved with an initial condition of ray having $P = P_0(x_0, y_0, z_0)$ and $T = T_0(Tx_0, Ty_0, Tz_0)$. Starting from the initial point (P_0, T_0), one can trace a ray path through the GRIN medium using the Runge–Kutta algorithm which can be written as eqs 6, 7, and 8

$$P_{n+1} = P_n + \Delta t\{T_n + (A + 2B)\} \tag{6}$$

$$T_{n+1} = T_n + (A + 4B + C)/6 \tag{7}$$

where

$$\begin{aligned} A &= \Delta t D(P_n) \\ B &= \Delta t D(P_n + \Delta t T_n/2 + \Delta t A/8) \\ C &= \Delta t D(P_n + \Delta t T_n + \Delta t B/2 \end{aligned} \tag{8}$$

First, we calculated the refraction of the injected ray that is parallel to an optical axis of the lens at an anterior surface of GRIN lens. After determining P_0 and T_0, the ray trajectory inside the GRIN medium was numerically traced successively (P_0, T_0), (P_1, T_1),

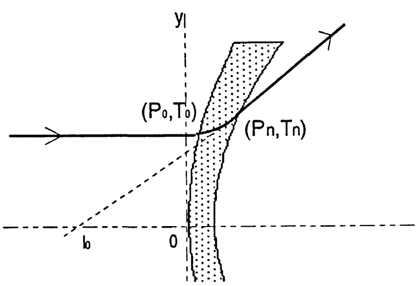

Figure 4. Ray trajectory of the GRIN material.

$(P_2, T_2), \cdots, (P_n, T_n)$ according to the above procedure. The position and direction vectors of the ray at a posterior surface of GRIN lens were determined. The power of the GRIN lens was estimated by calculating the position "l_0" at which the extrapolated line of ray after the lens crosses an optical axis as shown in Figure 4.

ESTIMATION OF FOCUSING PROPERTIES THROUGH GRIN LENS

The focusing power of the conventional lens is determined by the following parameters: curvature radius of anterior surface (R_1), posterior surface (R_2), thickness of lens (d) and the refractive index of the medium. In the case of the GRIN lens, the function of index distribution is added to the above parameters, increasing the freedom of controlling focusing properties.

In order to quantitatively estimate the advantages of the large GRIN lens such as in Figures 2 and 3, the following simulation was made: It was assumed that the refractive index distribution is expressed by eq 9

$$n(r) = n_0 + Ar^2 \tag{9}$$

where A is a constant of the refractive-index distribution.

Here $R_1 = 117.6$ mm, $R_2 = 69.0$ mm, radius (R_p) = 40 mm, and $d = 1.5$ mm which is the typical dimension of eyeglasses having the diopter $D = -3.0$ ($D = 1/f$, f: focus length in meter). Figure 5 shows the calculated results of the diopter with radial distance r from the center of lens. When $\Delta n = 0$ that is the conventional lens having a constant refractive index, the diopter gradually decreases with increasing the r. This means that the focal point depends on the incident position of injected ray, showing spherical aberration.

In general, the spherical aberration can never be eliminated by conventional index constant lenses with simple spherical curvatures. On the

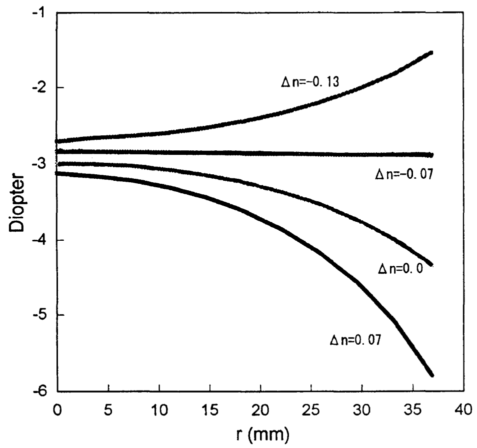

Figure 5. Diopter with r for the large GRIN polymer lenses. $R_1=117.6$ (mm), $R_2=69$ (mm), $d=1.5$ (mm).

other hand, it is quite noteworthy that when $\Delta n \equiv n(R_p)-n_0=-0.07$, diopter of -3.0 is constant with r, which means that the GRIN lens has no spherical aberration. In the case of $\Delta n=0.07$, the diopter dramatically decreases with increasing r, which suggests the possibility of preparing multifocusing lenses maintaining simple spherical curvature of lens. The large radial GRIN polymer lens will provide great advantages to ophthalmic lenses and other large lenses.

CONCLUSIONS

The curved mold method for preparing a very large GRIN polymer plate is proposed. By using this method, the resulting radial-GRIN plate had a diameter 70 mm of the GRIN region and Δn of 0.02. The specified combinations of the monomers and molds make it possible to obtain many large GRIN polymers with different Δn and different index profiles.

The ray analysis based on Maxwell's ray equation suggests that such large radial GRIN lens will provide great advantages into large optics such as ophthalmic lenses.

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