Journal of the Taiwan Institute of Chemical Engineers 43 (2012) 301–305

Contents lists available at SciVerse ScienceDirect

Journal of the Taiwan Institute of Chemical Engineers

journal homepage: www.elsevier.com/locate/jtice

Gel effects on the fabrication of gradient refractive index plastic rods via energy-controlled polymerization

M.J. Niknam Jahromi, Jui-Hsiang Liu *

Department of Chemical Engineering, National Cheng Kung University, Tainan 70101, Taiwan

ARTICLE INFO

Article history:
Received 20 April 2011
Received in revised form 16 August 2011
Accepted 23 August 2011
Available online 23 September 2011

Keywords:
Optics
Photopolymerization
Photorefractive effect
Refractive index
Radical polymerization

ABSTRACT

A UV energy-controlled exposure process for the fabrication of gradient refractive index lenses was developed. In the proposed method, a V-shaped gel zone was formed in the reaction tube to prevent the formation of bubbles in the polymer matrix after photo-induced polymerization. Gel effects on the fabrication and properties of GRIN polymer rods were clarified, and the effect of concentrations of diphenyl sulfide, poly(methyl methacrylate) and photoinitiator on the optical properties of the rod lenses were investigated. A convenient method for the fabrication of gradient refractive index (GRIN) lenses via a UV energy-controlled process using a sloped UV lamp is described, and theoretically available equipment similar to the sloped UV-controlled polymerization system is also proposed.

1. Introduction

Gradient refractive index (GRIN) lenses can be used to control the optical properties of materials and allow for more flexible optical designs compared to that of conventional homogeneous media. Interest in GRIN lenses has increased due to their ability to reduce spherical and chromatic aberrations [1,2]. GRIN has been used in various applications, such as rod lenses, fiber couplers and optical fibers [3–7].

A gradient refractive index (GRIN) lens is a cylindrical medium with a parabolic refractive distribution. Specifically, in a GRIN lens, the refractive index is highest on the optical axis of the rod and decreases toward the periphery as the square of the radial distance from the optical axis decreases [8–10]. GRIN optical lenses have been widely used in image transmission systems and high density information transmitting systems, including the sensor head of copy machines and facsimiles and internet connections in school campuses and sets of buildings [11–13]. With respect to the preparation process, equipment cost and material cost, GRIN plastic lenses have many advantages over GRIN quartz lenses, and can potentially be used in short distance information transmitting systems [14–19]. The gel effect is a phenomenon that often occurs during free radical polymerization at high degrees of conversion and results in the auto-acceleration of the rate of the polymerization. The gel effect is due to diffusion limitations that slow down termination but do not alter the rate of propagation and initiation [20–22].

Lots of functional polymers were synthesized and studied for applications in humidity sensor [23], biosensor [24], and biomaterials [25]. Controlling of polymerization processes has been regarded as a new class of materials for many new electronic, optic or magnetic applications, since many bulk properties can be significantly improved. In need to solve many shortcomings, photo-polymerization, which is one of the most interesting types toward better optical characteristics, such as reliability, ease of processing and low fabrication cost. Recently, GRIN lenses with quadratic refractive index distributions that vary continuously from the optical axis to the periphery have been studied due to their potential applications in self-focusing imaging and optical communications [26,27]. Several methods have been used to prepare GRIN lenses, including two-step copolymerization [28,29], extrusion [30], interfacial-gel copolymerization [31], photopolymerization, and swollen-gel polymerization [32].

In our previous communication, we reported a novel method for the fabrication of gradient refractive index plastic lenses using a sloped UV lamp via an energy-controlled process [33]. Due to the use of controlled UV energy, light-induced polymerization occurred from the bottom up, leading to the formation of a bubble-free gradient refractive index plastic rod. In this paper, we demonstrate the energy-controlled effect on the fabrication and the characteristics of GRIN lenses synthesized through this novel method. Moreover, we propose similar UV energy-controlled equipment for the fabrication of GRIN lenses.

---

* Corresponding author. Tel.: +886 953 655768.
E-mail address: jhliu@mail.ncku.edu.tw (J.-H. Liu).

1876-1070/$ – see front matter © 2011 Taiwan Institute of Chemical Engineers. Published by Elsevier B.V. All rights reserved.
doi:10.1016/j.jtice.2011.08.006

2. Experimental

2.1. Materials

Ciba IRGACURE 184 (1-hydroxy-cyclohexyl-phenyl-ketone) was used as a photoinitiator. Methyl methacrylate (MMA), which presented a refractive index of 1.41, and poly(methyl methacrylate) (PMMA), which displayed a refractive index of 1.49, were purchased from Tokyo Chemicals (TCI, Japan) and were used as a monomer and polymer, respectively. The diphenyl sulfide used in the current investigation presented a refractive index of 1.6325 and was used as a nonreactive dopant. Hydroquinone in the monomer was removed by washing with alkali solution.

2.2. Analysis apparatus

The refractive index profile of GRIN rods was measured with a York-P102 profile analyzer, and the refractive index of the matching oil was 1.458. The images obtained through the GRIN polymer rods were recorded on a camera equipped with an enlarging lens. The inhibitor present in the monomer was removed by washing with alkali solution, and the monomer was subsequently distilled under vacuum. The acceptance angle of GRIN lenses was estimated by transmitting real images through the rod lenses.

2.3. Preparation of GRIN plastic optical rods [34]

A mixture of methyl methacrylate (MMA), diphenyl sulfide (DS), and PMMA with a predetermined amount of acrylic polymer and Ciba IRGACURE 184 (1-hydroxy-cyclohexyl-phenyl-ketone) was poured into a Pyrex glass tube. Subsequently, the tube was capped and vertically rotated at 20 rpm. As shown in Fig. 1, a germicidal UV lamp (10 W, λ_{max} = 254 nm) equipped with a small slope angle (θ = 7.6° to vertical) was used as a source of UV light. Due to the distribution of incident light, the bottom of the reactor tube received a higher dose of energy. In this investigation, a Pyrex glass tube was used as the reactor. After polymerization, the glass tube was scored with a diamond cutter. A melted glass ball was placed in direct contact with the scored edge to break the glass tube, and the GRIN lens was removed.

3. Results and discussion

3.1. Fabrication of GRIN rods

Fig. 1 shows a schematic representation of the equipment used in the UV-controlled polymerization of plastic rods. The UV lamp was equipped with a small slope angle (θ = 7.6° to vertical), and the energy from the sloped UV lamp was incoherent. The strongest energy was emitted to the bottom of the tube, and the strength of the energy decreased gradually from the bottom to the top of the reactor, as indicated by the dark area shown in Fig. 1. As a result, a gel zone formed in the reaction tube and is shown as a V-shaped curve in zone B. As shown in Fig. 1, the monomer mixture in zone A did not receive enough energy for a polymer gel to form along the glass wall. However, the monomer present in zone C was almost completely polymerized into a gel.

As shown in Fig. 1, a V-shaped distribution of gel was observed as the reactor continued to receive UV irradiation, resulting in the gradual formation of a polymer from the periphery to the center of the rod. Moreover, due to the polymerization geometry, most of the nonreactive diphenyl sulfide (DS) was pushed toward the central axis of the rod. The final distribution of DS in the polymer matrix produces the desired gradient refractive index profile. Shrinkage due to the polymerization of monomers in the matrix was offset by the presence of an upper layer of liquid monomer. Because polymerization involves the binding of monomer, this process usually draws monomer molecules closer together, resulting in matrix shrinkage. If monomers do not accumulate in zone B (Fig. 1), a gel rod with bubbles will be produced by the polymerization reaction. Through the proposed process, a bubble-free gel rod was formed via primary-controlled UV polymerization and was subsequently heated at 60 °C for 24 h to completely polymerize the monomers in the rod.

Fig. 2 shows one half of the glass reactor during the UV-induced polymerization of the monomer mixture. As shown in Fig. 2(a), in the first stage of the reaction, the monomer mixture was homogeneous. However, after a certain amount of UV radiation was received, polymerization began from the bottom and periphery to the top and center of the glass reactor due to the energy distribution shown in Fig. 1, resulting in the formation of a V-shaped gel zone. Fig. 2(c) shows the final product of the reaction: a bubble-free gradient refractive index plastic rod.

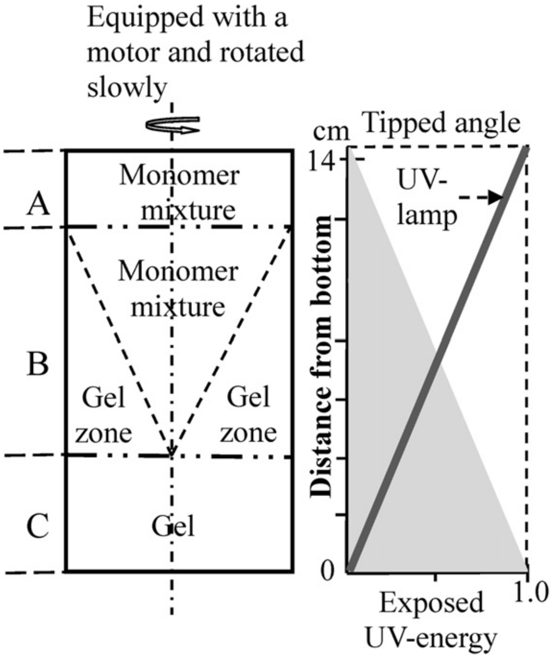

Fig. 1. Schematic representation of the equipment used in the UV-controlled polymerization of GRIN lenses.

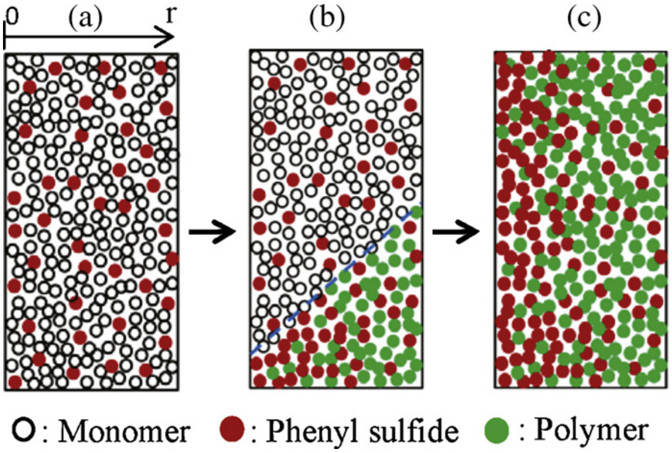

Fig. 2. Schematic representation of controlled energy polymerization in the glass reactor. One half of the system is shown.