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A novel method for preparing gradient index (GI) plastic rods

Initiator diffusion technique

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Summary

The initiator diffusion technique was used in this study to prepare the gradient index(GI) plastic rods, in which two kinds of initiators were used, i.e., thermal initiator and redox initiator. Experimental results showed that a GI plastic rod with a parabolic profile of refractive index was obtained by the initiator diffusion technique. The difference of the refractive index from the center to the periphery (Δn) of the plastic rods was in the range of 0.004-0.014. Δn increased with increasing temperature due to the increase of the gel effect and diffusion rates of monomers at a higher temperature. Furthermore, the GI plastic rod had substantially less defects, e.g., bubbles and opaqueness, than that prepared from interfacial-gel copolymerization.

Introduction

Gradient Index (GI) polymers have recently attracted extensive attention in light of their highly promising potential in optical fiber communication and microoptics(1). The refractive index varies continuously within the gradient index polymeric materials. This variety allows them to have unique optical properties that conventional optical materials with constant refractive index cannot achieve. Equation (1) shows an expression of the

$$n(r) = n_c(1-1/2Ar^2)=n_c(1-1/2A'(r/r_p)^2) \qquad (1)$$

refractive index distribution of a GI plastic rod, 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 and A' are distribution constants. Koike et al. reported a GI polymer optical fiber with a high bandwidth of 2 GHz.km while that of a step-index polymer optical fiber was only 5 MHz.km(2). The Selfoc Lens Array(SLA) made from GI polymers is used commercially in fax machines for 1:1 image transfer (1).

Several synthetic approaches have been used to prepare the gradient index polymers, e.g., two-stage copolymerization(3), photocopolymerization(4), centrifugal molding(5), interfacial-gel copolymerization(6-8), and vapor phase diffusion copolymerization(9). The differences between the monomer concentration, monomer reactivity, and monomer size were the driving forces behind producing index gradient

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inside the polymers. In the case of 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) . In this study, a new method is presented for preparing the GI plastic rods via the initiator-diffusion technique. This method basically modifies the interfacial-gel copolymerization technique. The initiator diffusion technique allows for control of the reaction direction as well as the refractive index profile. Two types of initiators were used in this study, i.e., thermal and redox initiators. BPO was used singly as the thermal initiator. The redox initiators can polymerize the reaction mixture at low temperature such as 40°C, thereby resulting in the reduction of shrinkage in the polymeric rods. Benzyl peroxide(BPO) with N,N'-dimethylaniline(DMA) were used as the redox initiator(10). The effect of the gel state on the value of Δn was also studied.

Experimental

1. Materials

Methyl methacrylate(MMA)(99%, Jassen), benzyl methacrylate(BzMA)(98%, TCI), benzyl peroxide(BPO)(98%, Jia Hwa Chemical, Co.), N,N'-dimethylaniline (DMA)(99%, TCI), and poly(methyl methacrylate)(PMMA)(Chi Mei) were used without further purification.

2. Preparation of GI rods

2.1 Principle of forming GI plastic rods

The monomer mixture was MMA and BzMA, which have similar reactivity ratios and refractive indices of 1.49 and 1.56, respectively. The mixture was filled into a PMMA tube. The inner wall of the PMMA tube was slightly swollen by the mixture and then formed a gel phase. MMA, which has a smaller size than BzMA, can penetrate into the gel phase easier than BzMA. Therefore, the BzMA monomer with a higher refractive index is gradually concentrated in the center region of the tube while the MMA monomer is accumulated in the periphery of the tube. Instead of mixing the initiator with the monomers reported by the interfacial-gel copolymerization, the initiators were coated on the surface of PMMA tubes. The initiators were then gradually diffused into the mixture of the monomers and the mixture was subsequently polymerized resulting in plastic rods with gradient indices.

2.2 Coating of PMMA tubes

3% of BPO, and 30% of PMMA were mixed with 26 ml of MMA in a 50 ml flask. The mixture was stirred by a magnetic stirrer until PMMA was completely dissolved. 6 g or 10 g of the mixture were poured into a PMMA tube which had a length of 28.7 cm and the outside and inside diameters were 15mm and 11mm, respectively. The tube was then rotated by a rotating coating machine at a speed of 90 rpm. Thus, thin films with the thickness of 0.5 and 1 mm were coated on the PMMA tubes for 6 and 10 g of samples, respectively.

2.3 Polymerization

The PMMA tubes coated with initiators were sealed by silicon rubber on one side. For the redox initiator system, a monomer mixture of 20 ml of MMA, 5 ml of BzMA, and 0.43% DMA were poured into the PMMA tubes. In the case of the thermal initiator, DMA was not added into the monomer system. The PMMA tubes were placed into a water bath with a constant temperature of 70^0C, 40^0C, and 60^0C for samples a, b, and c, respectively. After 8 hours, the tubes were placed into a vacuum oven at 100^0C for another 8 hours. The weight of the coated mixture, reaction temperature, and the difference of the refractive index from the center to the periphery of the plastic rod for samples a, b, and c are listed in Table 1.

Table 1. The weight of the coated mixture(W), reaction temperature(T), and difference of the refractive index from the center to the periphery (Δn) for samples a, b, and c.

Sample	W(g)	T(^{0}C)	Δn
a	10	70	0.014
b	6	40	0.004
c	6	60	0.01

3. Characterization

The refractive index profiles of the GI 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.

Results and Discussion

1. The thermal initiator system

Figure 1 shows the profile of the refractive index of sample a , which was prepared by using a thermal initiator (BPO) at a polymerization temperature of 70^0C. The distribution of the refractive index was a parabolic type and the difference of the refractive index from the center to the periphery (Δn) of the sample was 0.014, which was close to the value obtained from interfacial-gel copolymerization using the same reaction condition(6-8). The constant A' obtained form the curve fitting of equation (1) was $1.56\text{x}10^{-2}$. Besides, the GI plastic rod prepared by the thermal initiator system was transparent and contained one or two tiny bubbles. This preparation was relatively difficult to achieve in our previous study on the preparation of GI rod by interfacial-gel copolymerization using the same reaction condition(8), which contained either a bubble with a length 1 to 5 cm or many tiny bubbles or in some cases would be opaque. The defect of the opaqueness in the GI plastic rod was caused by phase separation from the homopolymerization of MMA or BzMA. This defect was eliminated in the initiator diffusion technique and hence a true copolymer consisted of BzMA and MMA was formed in the plastic rod. Hence, we can conclude that the GI plastic rod prepared by the thermal initiator system obtains a reasonably high Δn and without opaqueness.

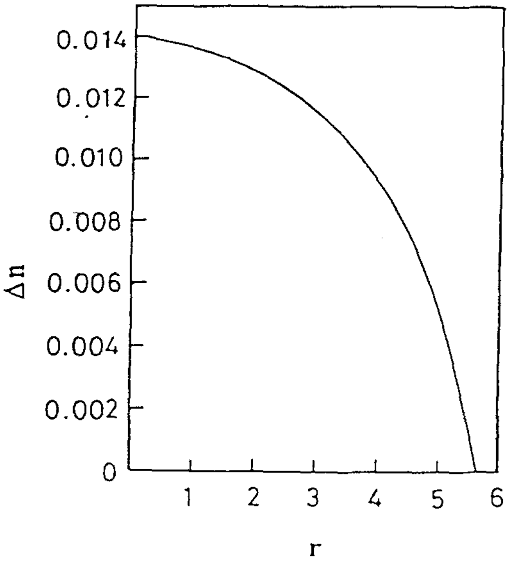

Figure 1 The relationship between the difference of the refractive index(Δn) and radius (r) for sample a.

2. The redox initiator system

The distribution of the refractive index of sample b using the redox initiator system was also a parabolic type and the values of Δn and A' were 0.004 and $5.56\text{x}10^{-3}$, respectively. The lower Δn of sample b was probably due to the insignificance of the gel effect and the lower diffusion rate of monomers at a lower temperature. The polymerization, which occurred at the low temperature by the redox initiator reduced the reaction rate, thereby decreasing the shrinkage of the polymeric rods. Hence, a GI polymeric rod without bubbles was obtained. Also, the rod was transparent. When the temperature increased from 40^0C to 60^0C in sample c, Δn increased to 0.01 with the same concentration of the initiator. The increase of the temperature accelerated the gel effect and diffusion rates of monomers and resulted in a higher Δn. Hence, we conclude that the system of the redox initiator could be used to obtain defect-free plastic rods and Δn was significantly affected by gel effect and diffusion rate.

Conclusions

Gradient index plastic rods were prepared in this study by the initiator diffusion technique. This technique could not only obtain a parabolic profile of the refractive index but also achieve a GI plastic rod with fewer defects than interfacial-gel copolymerization. The differences of the refractive index between the center and the periphery of the plastic rod by the initiator-diffusion technique were in the range of 0.004-0.014. Δn was significantly affected by the gel effect and diffusion rate of the monomers. The increase of the reaction temperature increased the gel effect and diffusion rate and resulted in a higher Δn.

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