Preparation of Heat-Resistant Gradient-Index Polymer Optical Fiber Rods Based on Poly(*N*-isopropylmaleimide-co-methyl methacrylate)

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ABSTRACT: Using the interfacial gel polymerization method, a heat-resistant gradient-index polymer optical fiber (GI POF) was developed based on the copolymer of methyl methacrylate (MMA) and *N*-isopropylmaleimide (IPMI) as the matrix material and bromobenzene (BB) as dopant. The gradient distribution of IPMI in the GI POF rod was determined by element analysis. IPMI had great advantage in improving glass transition temperature (T_g) and forming a gradient-index profile. There was a significant enhancement in the heat-resistant property in comparison with a conventional GI POF rod. The combination of high thermal stability and easy fabrication makes the novel BB–IPMI–MMA system very suitable for heat-resistant GI POF. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 87: 280–283, 2003

Key words: copolymerization; fibers; refractive index; thermoplastics; optics

INTRODUCTION

Polymer optical fibers (POFs) have attracted considerable interest for their versatile applications because of their good flexibility, ease of handling, and low cost.[1–5] The POF developed so far has been divided into two classes of structure: one is of step index (SI) type and the other is of gradient-index (GI) type. The bandwidth of transmission of SI POF is limited because of modal dispersion. In contrast, GI POFs have a much higher bandwidth, so they can meet the requirement in modern high-speed data links systems rather than SI POFs.

Usually, poly(methyl methacrylate) (PMMA) is applied as the core material of POF. However, one major drawback of PMMA is its relatively low glass transition temperature (T_g), which limits the usefulness of conventional POFs based on PMMA to a maximum temperature close to 85°C. With the spread of fiber optic technology, there is a great demand for POFs with high thermal stability for use in, for example, communication networks in factory buildings or vehicles. To obtain heat-resistant POFs, polymers with high T_gs have been chosen as core material; such as, highly crosslinked polycarbosiloxane.[6] Although SI POFs with high thermal stability were successfully fabricated with these materials, difficulty in preparing GI POF will confine their application. Recently, a method was proposed to improve the thermal stability of GI POF by selecting suitable dopant material and decreasing the dopant concentration;[7–9] however, the vital problem of low thermal stability of matrix could not be solved in this way. To date, there has been no satisfactory method to fabricate a heat-resistant GI POF.

The copolymer of methyl methacrylate (MMA) with *N*-substituted maleimide has been known as one of the superior resins in light of its thermal stability and transparency. In particular, *N*-substituted maleimide bearing an aliphatic or alicyclic group has drawn attention as a monomer because this type of compound affords a heat-resistant resin by copolymerization without damaging the characteristics of the original homopolymer of MMA.[10,11] In the present work, *N*-isopropylmaleimide (IPMI) was chosen as comonomer with MMA because of its convenient purification and good miscibility. The copolymer of MMA and IPMI provides a transparent and colorless heat-resistant resin.

This article describes a new method for preparing a heat-resistant GI POF rod by an interfacial-gel copolymerization technique, with the copolymer of MMA and IPMI as the matrix material and bromobenzene (BB) as the dopant. The distribution of IPMI in the rod was determined. The improvement in the heat-resistant property of the GI POF rod based on this BB–

IPMI–MMA ternary system was investigated. We found that IPMI played two roles in this system: one is to improve the T_g of the MMA–IPMI copolymer; the other is to associate BB to form quadratic refractive index distribution. To the best of our knowledge, heat-resistant GI POF of this kind is reported here for the first time.

EXPERIMENTAL

Materials

Methyl methacrylate (MMA) was purified by washing with 5% NaOH solution, then with distilled water until neutral. The washed monomer was dried over anhydrous Na_2SO_4, and then distilled under reduced pressure. *N*-Isopropylmaleimide (IPMI) was synthesized according to the procedure reported by Yuichi Kita et al.[11] and recrystallized from xylene. Bromobenzene (BB) was distilled twice. Azobisisobutyronitrile (AIBN) was recrystallized from alcohol. *N*-Butylmercaptan (nBM) was used as chain transfer agent, without further purification.

Preparation of GI POF rods

The preparation of GI POF rods was basically by the method of Koike et al.[1–4] The monomer mixture of MMA and IPMI, the initiator, and the chain transfer agent were fed into the PMMA tube prepared in our laboratory; the outer and inner diameters of the tube were 11 and 6 mm, respectively. The PMMA tube filled with the monomer mixture was placed in a furnace at 75°C for 48 h, followed by a postpolymerization at 95°C for 48 h.

Measurement

The GI POF rods were lathed layer by layer in a proper step along the radial direction and specimens of each layer were collected. Then, the content of nitrogen of each specimen was measured with a Carlo Erba-1106 element analyzer. In this experiment, one prepared GI POF rod was cut into five portions along the radial direction. Glass transition temperatures (T_g) were determined with a TA-2910 differential scanning calorimeter. The T_g was defined as the midpoint of the differential scanning calorimetry (DSC) curve. The refractive index profiles of the prepared GI POF rods were measured with a York P 104 profile analyzer, in which a piece of quartz crystal with a refractive index of 1.4587 was used as the reference.

RESULTS AND DISCUSSON

Distribution of IPMI

To determine the distribution of IPMI from the periphery to the center, element analysis of nitrogen was
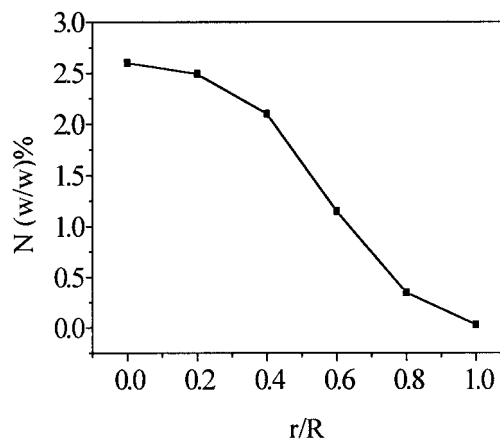

Figure 1 Distribution of N element of the IPMI–MMA system preform. The contents of IPMI and nBM in the polymerization solution are 20 wt % and 0.015 mol/L, respectively.

performed, and the amount of IPMI at different points along the radial direction was calculated from the nitrogen content. Here, BPO was used as the initiator instead of AIBN, because of the nitrogen in AIBN. The distribution of IPMI of the rods prepared by interfacial gel copolymerization method is shown in Figure 1. The IPMI distributed with a gradient concentration across the section of the rods. This result is due to the difference of monomer reactivity ratio between MMA (M_1) and IPMI (M_2) for the copolymerization, which have been evaluated as $\gamma_1 = 1.72$ and $\gamma_2 = 0.17$,[11] respectively. Generally speaking, in the polymerization processes, when a gel phase is formed from the inner wall of the PMMA tube, the rate of the polymer reaction in the gel is faster than in the monomer liquid phase. Therefore, copolymer thickens from the periphery to the center. Meanwhile, MMA is first preferentially polymerized in the gel phase because of the difference in monomer reactivity of MMA and IPMI. Therefore, the composition of the copolymer formed during polymerization gradually changes; in the other words, the fraction of IPMI increases from the periphery to the center. A similar mechanism has been previously discussed.[3]

Effect of IPMI on T_g

It is well known the introduction of a rigid structural unit into the main polymer chain improves T_g. The rigid structural units of IPMI in the MMA–IPMI copolymer backbone therefore resulted in an increase in T_g. The relation between the content of IPMI and T_g of the GI POF matrix material is shown in Figure 2. The T_g increased with the increasing content of IPMI. Because a chain transfer agent was added, which is necessary for the heat-drawn POF, T_g values in this test are lower than those previously reported.[11]
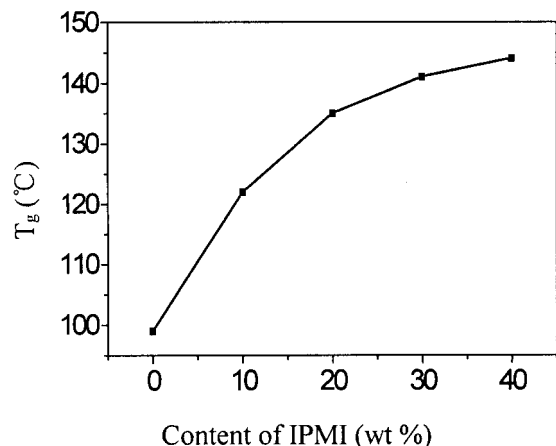
Figure 2 Relationship between IPMI concentration and T_g of the IPMI–MMA copolymer. The content of nBM is 0.015 mol/L.

Figure 4 Comparison of T_g between the IPMI–MMA system GI preform and the conventional GI preform. Key: (A) 20 wt % IPMI and 14 wt % BB-doped GI preform; (B) 20 wt % BB-doped conventional GI preform.

Effect of IPMI on refractive index profile

Materials that can be used as dopant in the interfacial gel method should satisfy the following two conditions: a higher refractive index and a lower reactivity. The refractive indices of IPMI and MMA are, respectively, 1.474 and 1.412.[10] Furthermore, as already mentioned, the reactivity ratio of MMA (M_1) is higher than that of IPMI (M_2), and so it is possible for IPMI to be used as a dopant. This prediction was confirmed, as shown in Figure 3, by the quadratic-like index profiles of all the rods. The feed content of IPMI strongly influence the difference of the refractive index (Δn) between the center and the periphery of these rods: Δn increased with the increasing concentration of IPMI. It is obvious that IPMI has the same effect as dopant on the refractive index profile.

Unfortunately, mistiness appeared in the prepared rods if the concentration of IPMI was >30 wt % in the polymerization solution. This problem probably resulted from phase separation due to the homopolymerization of MMA or IPMI. A feed concentration of 20 wt % of IPMI was chosen in this work, and the rods were completely transparent. However, at this concentration, Δn isn't high enough to satisfy the requirement of GI POF, and bending loss should be induced. Therefore, a dopant (i.e., BB) was used to associate with IPMI to obtain a higher Δn value. In Figure 3, a preferable refractive index profile was also presented when 14 wt % BB was added. For a conventional GI POF rod to achieve the same Δn as shown in the curve E, at least 20 wt % of dopant concentration is needed. Both IPMI and BB have contributions to the gradient refractive index distribution profile in this BB–IPMI–MMA system, which results in a dramatic decrease in the feed concentration of the dopant. In addition, as shown in Figure 3, if the absolute value of Δn is below ~0.01, both IPMI and BB can be the dominant factor in forming the refractive index profile. However, because the concentration of IPMI is limited to <30 wt % in the polymerization solution, we have to rely on BB to form the refractive index profile with absolute value of Δn of >0.01; that is, BB will be the dominant factor if a higher Δn value is required.
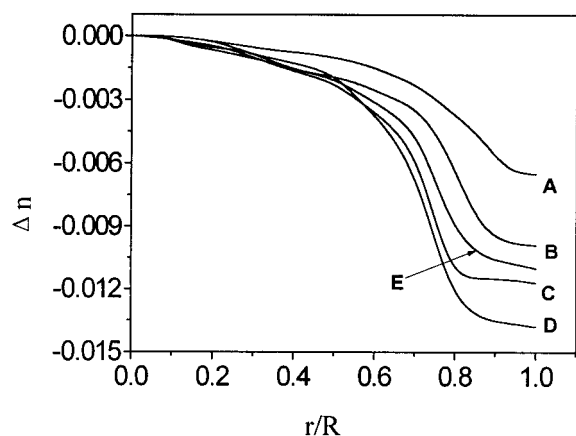

Figure 3 Relationship between IPMI concentration and refractive index distribution of the prepared preforms. Key: (A) 20 wt % IPMI; (B) 30 wt % IPMI; (C) 40 wt % IPMI; (D) 50 wt % IPMI; and (E) 20 wt % IPMI plus 14 wt % BB-doped specimen.
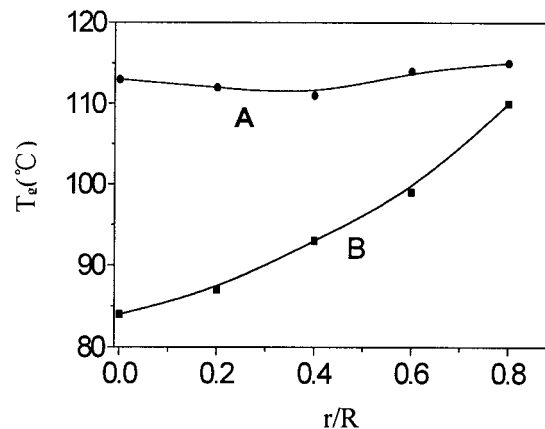
Improvement of thermal stability

The T_g values of different regions along the radial direction in the GI POF rod based on the BB–IPMI–MMA system are compared with those of the conventional rod in Figure 4. We know that the dopant works as plasticizer, and the dopant molecule strongly influences the thermal stability of the matrix.[9] Meanwhile, in the GI POF rod, the BB concentration increases gradually from the periphery to the center. This situ-

ation means that T_g along the radial direction will lower with the increasing BB. With the conventional GI POF rod, the corresponding curve in Figure 4 exhibits this trend. The T_g value has a minimum at the center region at ~70°C. In spite of the higher T_g value at the peripheral region, the thermal stability property at the center region would determine that of the whole GI POF. Hence, conventional GI POF should generally be used at temperatures <70°C. In the case of BB–IPMI–MMA system, we demonstrated that there is no minimum in the corresponding curve; that is, the T_g values in all of the regions are close to each other. One explanation for this result is that IPMI and BB have reverse effects on T_g. Furthermore, both IPMI and BB have similar distribution across the section of the rod, and therefore the counteraction of IPMI and BB results in the observed phenomenon. On the other hand, as previously mentioned, the low concentration of dopant has a great advantage in maintaining high T_g at center region. The results in Figure 4 suggest that the introduction of IPMI significantly enhances thermal stability of the GI POF rod in comparison to the BB–MMA system.

CONCLUSION

We have prepared heat-resistant GI POF based on a BB–IPMI–MMA system. Element analysis shows that IPMI had a gradient concentration distribution along the radial direction in the GI POF rods that is due to the difference in reactivity ratios between MMA and IPMI. The DSC studies and refractive index profiles confirm that IPMI not only increased the T_g of polymer materials, but also played an important role as dopant in the refractive index profile. In particular, the T_g in the center region of the BB–IPMI–MMA system GI POF rod is 115°C, which will effectively enhance the heat resistant property of GI POF in comparison with a conventional GI POF. Other properties are still under investigation.

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