

Refractive index distribution of graded poly(methyl methacrylate) preform described by self-diffusion approaches of free-volume theory in a ternary system

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Abstract

A series of graded index poly(methyl methacrylate) (PMMA) preforms with monomer/dopant = 5:1, 7:1, 10:1 have been made by an interfacial-gel polymerization procedure, in which polymerization was performed in a PMMA tube and a dopant, bromobenzene (BB), was used as a higher refractive index molecule. The graded index was formed by the diffusion of the molecules. While describing the process of interfacial-gel polymerization, the distribution of the polymer concentration at the radial direction of the tube was assumed to be $\omega = a(r/R)^2 + b$. According to the self-diffusion approach of the free-volume theory in ternary systems and its application in a high-conversion polymerization system, a model of forming the graded index is established, and a quadratic refractive index (RI) distribution on the cross-section of the preform is obtained. Compared with the theory in a binary system, the result is more identical with experiments in both the changing trend and the value of RI. The RI distributions of preforms prepared with different MMA/BB were simulated. The effect of MMA/BB on the RI distribution was also discussed. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Graded index polymer optical fibers; Interfacial-gel polymerization; Self-diffusion approach

1. Introduction

Polymer optical fibers (POFs) have received extensive interest due to their potential application in optical communication in recent years. Compared with glass fibers, POFs have certain advantages in some cases, such as good flexibility, light weight, large core diameter, high numerical aperture, low melting temperature, and low processing cost [1,2]. In particular, a large core diameter (such as 0.5 mm or more) makes POFs better transmitting media in the Local Area Net (LAN) because there would be many junctions and connections in such short distance communications and a fine core of silica optical fibers will be very expensive and difficult to utilize.

There are two types of POFs attributed to their different distributions of the refractive index (RI), namely, Step Index POFs (SI POFs) and Graded Index POFs (GI POFs). However, all commercial available POFs have been SI ones whose bandwidth of transmission is limited to about 50 MHz achieved in 100 m due to large modal dispersion

[3]. The narrow bandwidth of SI POFs has confined the use of POFs only to light guides and illumination components. It is well known that with GI POFs a high degree of equalization of the group velocities of the fiber modes became possible, so that the bandwidth available with multimode fibers was greatly increased [4]. The index distribution is often expressed by a power law of a form

$$n(r) = n_0[1 - 2(r/R)^g \delta]^{1/2} \quad (1)$$

where $n(r)$ and n_0 are the refractive indices at a distance r from the center and at the center axis, respectively. The parameter g is the exponent of the power law, and R the radius of the fiber core.

Two methods are often used to prepare GI POFs, one is the extrusion process [5], and the other is the process of drawing the preform, which is preparing the preform first and then drawing it into fiber under suitable conditions [6]. The GI POF preform could be successfully prepared by different processes, namely, photocopolymerization [7], two-step copolymerization [8], and interfacial-gel polymerization [9], etc. Along with many other methods interfacial-gel polymerization is often used to obtain the GI POF preform. Generally speaking, there are two steps for preparing GI POFs by the methods of interfacial-gel

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polymerization: the first is the preparation of preforms, and the second is the drawing of the fiber. The graded index profile forms in the first step in which the preform is made by a process of interfacial-gel polymerization. During the polymerization, the radial graded index distribution comes from the radial concentration of a doped molecule, which is formed by doped molecules diffusing into a gel phase on the inner wall of the polymerization container, since the RI of the dopant is higher than that of the polymer.

In our previous paper a graded index poly(methyl methacrylate) preform was made by an interfacial-gel polymerization and a model was given in terms of the self-diffusion approach of the free-volume theory in a binary polymer–solvent system [10]. The self-diffusion coefficients of BB and MMA were calculated by ignoring the effect of the other component. Actually the system discussed was a ternary system, namely, BB, MMA and PMMA, and the three components interact with each other. In this paper the free-volume theory of self-diffusion in a ternary system is applied in predicting the GI profile of preforms. Compared with the theory in a binary system, the theory in a ternary system is most close to the real circumstance and made the explanation of the theory more reasonable. From the simulation results in a ternary system, it can be seen that the result is in more agreement with experiments in both the changing trend and the value of the RI than in the binary system [10].

2. Experimental

2.1. Polymerization

The tubes of PMMA are commercial samples produced by Xingguang Chemical Regent Factory in Beijing, with a 6-mm inner diameter and a 10-mm outer diameter. The other chemicals and solvents are commercial products and are used after purification by standard methods.

The PMMA tubes were sealed at one end and then filled with a solution composed of methyl methacrylate (MMA) as a monomer, azobis(isobutyronitrile) (AIBN, 0.01 mol/l) as an initiator, dodecyl mercaptan (0.03 mol/l) as a chain transfer agent, and a specified amount of bromobenzene (BB). The PMMA tube was placed in a glycerin bath with a constant temperature of 80°C for 1 h and then 70°C until the solidification was completed. After the solidification, the tube was placed into a vacuum oven at about 100°C for 2 h, and then a preform rod was ready for characterization.

A series of preforms made by different ratios of MMA/BB = 5:1, 7:1 and 10:1 were prepared in the same manner.

2.2. Characterization

The RI was measured by the oil immersion method. A series matching oils were used with the Δn of two adjacent oils being 0.003. The samples were then prepared by cutting

on the cross section of the preform rod, the diameter of which is about 0.1 mm. The sample was then placed on one side of a glass sheet and covered by a small piece of micro cover glass. A drop of matching oil was dripped and diffused all over the sample. The RI was determined by the Beche-line method on an Olympus polarization microscope. The accuracy of this measurement was in the range of ± 0.0015 .

3. Self-diffusion approach of free-volume theory in a ternary system

The free volume theory can be assumed to be valid when there is a sufficient amount of polymer contact (for example, when the domain of polymer molecules begin to overlap), on the basis of which the analysis of diffusion behavior in concentrated polymer solutions has been primarily developed [11]. In a general version of the free volume theory, it is supposed that the diffusion process depends on the probability that a molecule will obtain sufficient energy to overcome attractive forces and on the probability that a fluctuation in the local density will produce a hole of sufficient size so that the diffusing molecule can jump. The second probability is sufficient hole free volume for transport to occur.

It is generally assumed that the diffusion process is free-volume driven for temperature sufficiently close to the glass transition temperature of the system [12]. It is worth noting here that, at a given polymerization temperature, the limiting conversion for cessation of polymerization has been identified with the conversion at which the medium turned into glass [13]. Furthermore, it can be expected that diffusing molecules will distribute according to the conversion gradient in a closed system and the distribution of diffusing molecules will be done later as the polymerization continues. In our polymerization systems, there are three components: monomer, dopant and polymer. The distribution of diffusing molecules can be predicted by the distribution of their diffusion coefficients along the conversion gradient.

In the following discussion, the solvents will be defined as components 1 and 2, and the polymer as component 3. In addition, the concentration dependence of the partial specific volumes of components will be assumed to be negligible so that there is no volume change on mixing. Under this condition, it is easy to show that the equations of the free-volume theory proposed by Vrentas and Duda take the following form for the self-diffusion coefficients D_1 and D_2 of the two components in a ternary polymer system [14]:

$$D_1 = D_{01} \exp \left\{ - \frac{(\omega_1 \hat{V}_1^* + \omega_2 \hat{V}_2^* \xi_{13} / \xi_{23} + \omega_3 \hat{V}_3^* \xi_{13})}{\hat{V}_{FH} / \gamma} \right\}, \quad (2)$$

$$D_2 = D_{02} \exp \left\{ - \frac{(\omega_1 \hat{V}_1^* \xi_{13} / \xi_{13} + \omega_2 \hat{V}_2^* + \omega_3 \hat{V}_3^* \xi_{23})}{\hat{V}_{FH} / \gamma} \right\}, \quad (3)$$

$$\frac{\hat{V}_{FH}}{\gamma} = \omega_1 \left(\frac{K_{11}}{\gamma} \right) (K_{21} + T - T_{g1}) + \omega_2 \left(\frac{K_{12}}{\gamma} \right) (K_{22} + T - T_{g2}) + \omega_3 \left(\frac{K_{13}}{\gamma} \right) (K_{23} + T - T_{g3}).$$

Here, D_{0I} is the preexponential factor for the component, ω_I the mass fraction of component I , \hat{V}_I^* the specific critical hole free volume of component I required for a jump, and \hat{V}_{FH} the average hole free volume per gram of mixture; γ is an overlap factor which is introduced because the same free volume is available to more than one molecule. Also, the parameter ξ_{I3} represents the ratio of the critical molar volume of a jumping unit of the polymer. Finally, K_{1I} and K_{2I} are free-volume parameters for the component I , and T_{gI} the glass transition temperature of component I . Note that it is the hole free volume which is the quantity available for molecular transport since it is assumed in the theory that this part of the solution volume can be redistributed with no energy change.

In a previous paper, four assumptions were established in order to calculate the self-diffusion coefficient in a binary system [10]. The four assumptions will still be used in the application of the above formulations that are introduced in a ternary system. Eqs. (2) and (3) would serve as a basis for the prediction of the concentration dependence of the self-diffusion coefficients D_1 and D_2 of the ternary solution at a temperature T if the following parameters could be obtained from single component or binary system data: D_{0I} , ξ_{I3} , K_{1I}/γ and K_{2I} are directly related to the WLF constants of the solvent and polymer.

4. Establishment of a model for forming a graded index profile in interfacial-gel polymerization

In interfacial-gel polymerization, diffusion and polymerization are conducted simultaneously. It is well known that the polymerization is accelerated in the gel phase. Therefore the polymerization is faster in the gel phase which is near the inner wall of the tube than in the monomer solvent near the center of the tube. At a certain time, the limiting free volume, which is caused by the increasing viscosity, make the diffusion cease while polymerization continues. Then the inert dopant molecule concentration remains unchanged till the end of the polymerization. In order to predict the distribution of the graded index of the GI POF preform by the free-volume of self-diffusion in a ternary system, two molecules are considered, which are the inert molecule and the monomer. The distribution of their self-diffusion coefficients, D_1 and D_2 , should be obtained firstly by assuming the distribution of the polymer concentration at the time when

diffusion ceased, as shown in the following:

$$\omega = a(r/R)^2 + b \quad (4)$$

where ω is the mass fraction of the polymer, r the radial distance, and R the outer radius of the tube, a and b are parameters determined by different polymerization systems. According to the law of conservation of mass, the mass of one component is in direct proportion to its diffusion coefficient and the concentration of the two molecules is determined by their diffusion coefficient, respectively. So the concentration distribution of the inert molecule BB can be expressed as follows [15]:

$$\omega_{BB} = \frac{D_1}{xD_1 + yD_2} (1 - \omega). \quad (5)$$

Here, ω_{BB} is the concentration distribution of the inert molecule BB, D_1 and D_2 are the diffusion coefficients of the inert molecule and the monomer, ω is the polymer concentration gradient, and x and y are molar fractions of the inert molecule and the monomer in the initial state of the polymerization. From the equation above, the distribution of the concentration of the inert molecule BB along the radial direction can be obtained.

After the polymerization is completed, the inert molecule concentration distribution remains the same distribution which formed when the diffusion was ceased. Then in the system there are only two components, which are the inert molecule and the polymer. For a compatible system, the relationship between RI and compositions of the system can be theoretically correlated by the Lorentz and Lorenz formulation [16]

$$\frac{n^2 - 1}{n^2 + 2} = \frac{1}{V} [(R_{I1} - R_{I2})C_1 + R_{I2}] \quad (6)$$

in which

$$V = (V_1 - V_2)C_1 + V_2.$$

Here, n is the RI, C_1 the concentration of the dopant molecule, V the molar volume of the mixture, V_1 and V_2 are the molar volumes of the dopant molecule and the monomer unit of the polymer, and R_{I1} and R_{I2} are molar refractions of the dopant molecule and the monomer unit of the polymer, respectively. If Eq. (6) is modified, a relationship between n and C_1 can be obtained as follows:

$$n = \sqrt{\frac{2[(R_{I1} - R_{I2})C_1 + R_{I2}] + V}{V - [(R_{I1} - R_{I2})C_1 + R_{I2}]}}. \quad (7)$$

It is evident that the RI distribution as a function of radial distance can be simulated from Eq. (7).

5. Results and discussion

Different from other polymerization processes, interfacial-gel polymerization is carried out in a container composed of polymers that can be dissolved into monomers

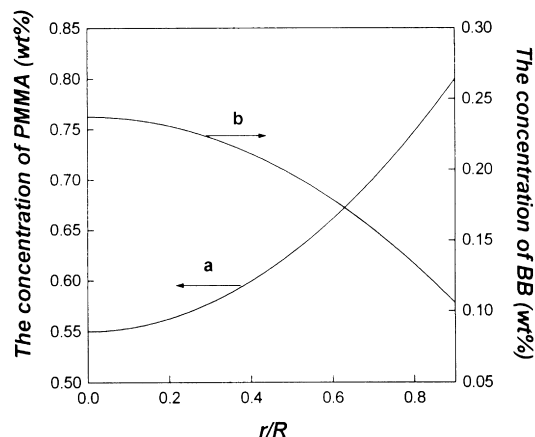


Fig. 1. Radical distribution of the concentration of: (a) PMMA; and (b) BB.

to be polymerized, such as polymer tubes. When the polymer tube is filled with monomers, the inner wall of the tube is slightly swollen and a gel phase is formed on the inner wall of the tube. It is well known that the polymerization is accelerated in the gel phase. Therefore, the polymerization is faster in the gel phase near the inner wall than in the monomer near the center of the tube. Under these circumstances the gel layer will gradually thicken in the center region as polymerization continues, and a gradient polymer concentration distribution forms along the radial direction of the tube. By optimization of polymerization condition, it has been known that at a certain time the polymer phase reaches the center axis of the tube and an equilibrium state is formed, in which the inert dopant concentration decreases monotonically from the center axis to the periphery. Although unreacted monomers will continue to polymerize in the gel layer, the volume condensation caused by conversion from monomers to polymers can only take place in the longitudinal direction of the reaction tube.

Interfacial-gel polymerization used in this work is a homopolymerization process in which a PMMA tube is filled with MMA monomer mixed with the polymerization initiator, the chain transfer agent, and one kind of molecule inert to the polymerization. BB ($n = 1.56$), which has a higher RI than the corresponding polymer, was selected as the inert molecule in the experiments.

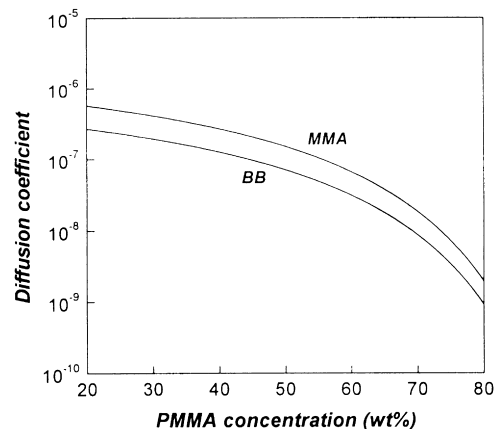


Fig. 2. The dependence of the diffusion coefficient of MMA and BB with the concentration of PMMA = 5:1 at the temperature of 80°C.

The detailed mechanism of forming the radial graded index distribution was reported in our previous paper [10], from which it has been known that the inert molecules were distributed with a gradient concentration along the direction of the radius contrary to that of polymers in the gel.

The RI distribution of the preform with a ratio of MMA/BB = 5:1 is simulated by the self-diffusion approach of the free-volume theory in a ternary system as an example. While working out the distribution of polymer concentration, the two parameters in Eq. (4) have to be determined firstly by boundary conditions. When the boundary conditions were assumed to be $\omega = 0.8$ at $r/R = 0.9$ and $\omega = 0.55$ at $r/R = 0$, according to Eq. (4) the distribution of PMMA concentration was obtained and is shown as Fig. 1a. It can be seen that the PMMA concentration increased slowly with the increase of the radial distance, and after reaching a certain distance, it increased rapidly with further increase of the radial distance.

The dependence of D_i on ω can be determined by Eqs. (2) and (3), if the following parameters are available: D_{0i} , \hat{V}_i^* , \hat{V}_{FH} , ξ_{I3} , K_{1I} , and K_{2I} , and T_{gl} , K_{1I}/γ . These parameters could be obtained from single component or binary system. The parameters needed for the evaluation of D_{MMA} and D_{BB} are presented in Table 1.

Using the data listed in Table 1, the dependence of D_{MMA}

Table 1
Vrentas–Duda free-volume parameters

	MMA	References	BB	References	PMMA	References
\hat{V}_I^* (cm ² /g)	0.87	[17]	0.591	[20]	0.757	[20]
$(K_{1I}/\gamma) \times 10^3$ (cm ³ /g K)	0.815	[19]	0.64	^a	0.477	^b
K_{2I} (K)	143	[19]	184.6	^a	52.38	^a
T_{gl} (K)	225	[22]	242.4	[20]	378	[21]
$D_{0I} \times 10^{-5}$ (cm ² /s)	4.07	^a	1.92	^a		
ξ_{I3}	0.60	[18]	0.60	[18]		

^a Calculated from the temperature dependence of MMA viscosity in Ref. [17] and BB viscosity in Ref. [20].

^b From the WLF constants in Ref. [23].

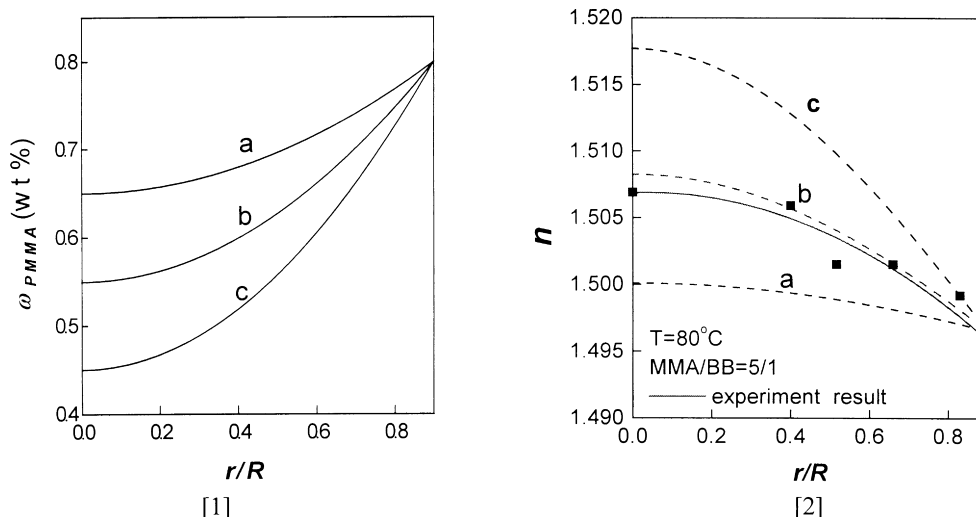


Fig. 3. The dependence of refractive index of the PMMA preform of MMA/BB = 5:1 at 80°C with different boundary conditions of the concentration of PMMA. The dotted curves (---) for theoretical simulation; the solid curves (—) for experimental results. The dots (B) are refractive indices measured by the experimental method: (a) $\omega_{r/R=0} = 0.45$, $\omega_{r/R=0.9} = 0.8$; (b) $\omega_{r/R=0} = 0.55$, $\omega_{r/R=0.9} = 0.8$; (c) $\omega_{r/R=0} = 0.65$, $\omega_{r/R=0.9} = 0.8$.

and D_{BB} on polymer concentration at 80°C was calculated by Eqs. (2) and (3). The result is illustrated in Fig. 2 and the result shows that the changing trends of D_{MMA} and D_{BB} values decrease gradually with the increasing of the concentration of PMMA. This means that with the increase of PMMA concentration, diffusion becomes more difficult. Because D_{MMA} is slightly larger than D_{BB} , MMA molecules can more easily diffuse into the gel phase than the BB molecules. Therefore, the BB concentration at the center region of the preform increased. The concentration distribution of BB in the radial direction can be obtained by Eq. (5), which is shown in Fig. 1b. It can be seen that contrary to the polymer distribution the concentration of BB decreases gradually from the center to the periphery of the tube.

After the concentration distribution of BB in the radial direction of the preform was obtained, with the data $R_{ll_1} =$

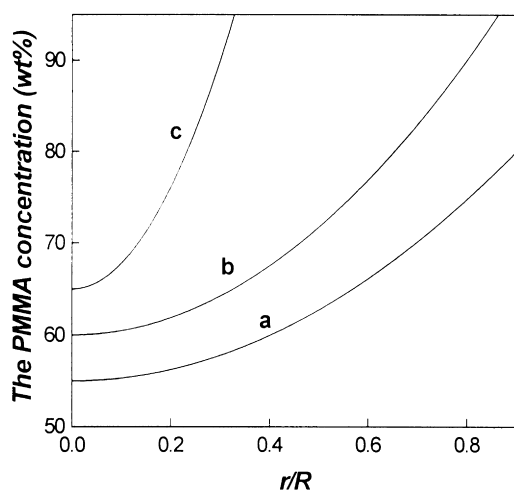


Fig. 4. The radical distributions of PMMA of different systems of MMA/BB: (a) MMA/BB = 5:1; (b) MMA/BB = 7:1; (c) MMA/BB = 10:1.

$34.407 \text{ cm}^3/\text{mol}$, $R_{ll_2} = 24.754 \text{ cm}^3/\text{mol}$, and $V_1 = 86.5 \text{ cm}^3/\text{mol}$, $V_2 = 104.71 \text{ cm}^3/\text{mol}$ calculated in terms of the method reported earlier [16], a predictive RI distribution with MMA/BB = 5:1 can be obtained and is shown as a dotted curve in Fig. 3-2b, from which it is easily found that the RI decreased with the increase of the radial distance.

In order to obtain the RI distribution which is in agreement with the experimental results, the boundary conditions of the polymer concentration have to be optimized. Fig. 3 gives the optimizing process for the polymerization system of MMA/BB = 5:1. Curves of a, b and c in Fig. 3-1 are of the same polymer concentration of 0.8 at $r/R = 0.9$, and different polymer concentrations at the center of the preform, which are 0.45, 0.55 and 0.65, respectively. Combined with these boundary conditions, the distribution of polymer concentration can be determined by Eq. (4). The RI distributions were simulated by the method described above and are shown in Fig. 3-2. The dotted curves show curves of simulated RI distributions given by the corresponding curves in Fig. 2-1. The solid curve is the result of the experiment. Compared with the experimental result, it can be seen that the boundary condition of $\omega = 0.55$ at $r/R = 0$ and $\omega = 0.8$ at $r/R = 0.9$ is suitable and shows that the theoretical model has good agreement with the experimental result.

For polymerization systems with different ratios of MMA/BB, the distribution of the concentration of the polymer would be different. According to the method described above, the polymer concentration distributions can be obtained first and are shown in Fig. 4 by curves a, b and c with MMA/BB ratios of 5:1, 7:1, and 10:1, respectively. The polymer concentration at the center of the preform is higher and the cladding region is thicker with increasing MMA/BB. Their RI distributions measured by the experimental method are shown as dotted curves a, b and c in Fig. 5.

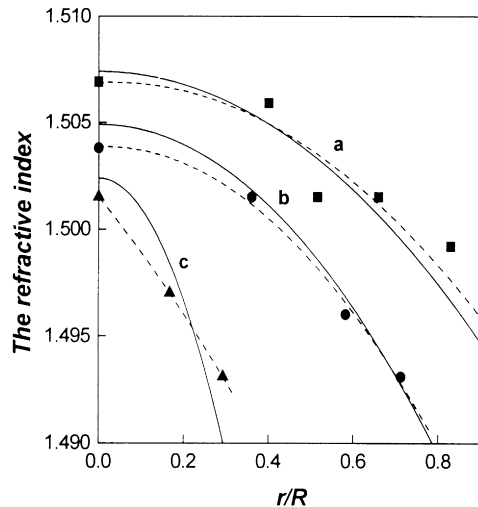


Fig. 5. The distribution of refractive index of the PMMA preform with different MMA/BB of the system of polymerization at 80°C: (a) MMA/BB = 5:1; (b) MMA/BB = 7:1; (c) MMA/BB = 10:1. The solid curves (—) for theoretical simulation; the dotted curves (---) for experimental results. The dots B, X and O are refractive indices, respectively, measured by the experimental method.

The solid curves in Fig. 5 give the corresponding theory simulations by self-diffusion approach in a ternary system. The corresponding index profile of the experiments of different ratios of MMA/BB is in good agreement with that of the corresponding profile predicted by the self-diffusion approach in a ternary system. Compared with the simulation results by the self-diffusion approach in a binary system, the agreement between the simulated and experimental curves is more satisfactory because the result is more

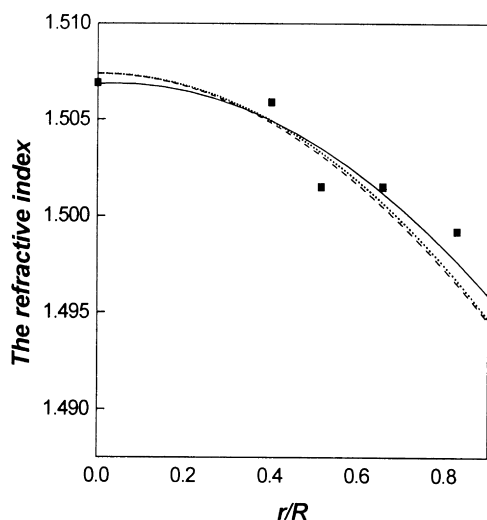


Fig. 6. The RI distribution of the preform of MMA/BB = 5:1. The dots (B) are experimental data; solid curves (—) for experimental simulation results; short dotted curve (· · ·) for theoretical simulation by the free-volume theory in a ternary system; dashed curve (---) for the power law expressed by Eq. (1).

identical with experiments in both the changing trend and the value of RI [10].

From Fig. 5 we can also see the effect of MMA/BB on the distribution of the RI of the preform. The preform with different MMA/BB has a parabolic profile of RI with the highest RI value at the center of the preform and the lowest at the periphery, which is called a cladding region. The RI at a certain distance from the center of the preform decreases and the cladding region become thicker with increasing MMA/BB. This can be explained by the fact that the BB concentration becomes lower with increasing MMA/BB and that the RI of BB ($n = 1.56$) is higher than that of PMMA ($n = 1.49$). When the BB concentration becomes lower, its diffusion ability drops so that the cladding region becomes thicker.

High bandwidth is one important characteristic for POFs to be applied in short-range communication systems [3]. It is well known that the bandwidth can be maximized by optimizing the shape of the RI distribution of the fibre [4], i.e. the bandwidth is maximized when the RI distribution is expressed by a power law of the form in Eq. (1) and without material dispersion g is simplified as follows [24]:

$$g_{\text{opt}} = 2 - \frac{12}{5} \delta \quad (8)$$

in which

$$\delta = \frac{n_0 - n_1}{n_0} \quad (9)$$

where n_0 and n_1 are the refractive indices of the core center and cladding, respectively. It has been confirmed that the RI profiles can be maintained throughout the fabrication process from a preform [25] and that the bandwidth is maximum when g is close to 2. The RI distribution expressed by the power law is calculated using the data in simulation. For the polymerization system of MMA/BB = 5:1, $n_0 = 1.5074$, $\delta = 0.0104$. In Fig. 6 the predicted RI distribution by the free-volume theory in a ternary system is shown by a short dotted curve and the RI distribution of power law by a dashed curve. From the results, it can be seen that the two curves are almost similar and no dispersion can be found. The experimental curve (solid curve) is also shown in Fig. 6. It can also be found that the theoretical simulation and power law curves are consistent with the experimental curve in both shapes and values. From analysis on this work it is easily deduced that the self-diffusion approach of the free-volume theory in a ternary system can be used to predict the RI distribution of the GI POF preform.

6. Conclusions

A series of preforms with a gradient RI distribution on the radial direction have been made by interfacial-gel polymerization. Diffusion and polymerization are conducting simultaneously in the polymerization process. At a certain time, the diffusion was ceased due to the limiting hole free

volume. Through the assumption of the polymer concentration and its boundary conditions, the distribution can be calculated in terms of the self-diffusion approach of the free-volume theory in a ternary system. Under these conditions, according to Lorentz and Lorenz formulation a quadratic distribution of RI on the radial direction of the preform is simulated. The theoretical model is more identical with the experimental results than that in a binary system. The ratio of MMA/BB would have a great influence on the distribution of the polymer concentration and the RI distribution. For polymerization systems with different ratios of MMA/BB, the polymer concentration distributions and the boundary conditions would be different. The simulation result is also consistent with the power law required by application of the GI POFs. Analysis on the results of this work has shown that the self-diffusion approach of the free-volume theory in a ternary system could be used to predict the RI distribution of the GI POF preform by assuming the polymer concentration distribution with optimized boundary conditions.

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