Refractive Index Distribution of Graded Index Poly(methyl methacrylate) Preform Made by Interfacial-Gel Polymerization

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ABSTRACT: A graded index poly(methyl methacrylate) (PMMA) preform has been made by a novel 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. A detailed mechanism of the graded index formation is given and simulated according to the free volume theory and its application in a high-conversion polymerization system. Under the assumption that polymer concentration distributes in the form of $\omega = a\ \exp(r) + b$ at the radial direction of the tube, a quadratic distribution of refractive index on the cross section of the preform is obtained. The result is identical with experiments performed by the interfacial-gel polymerization.

Introduction

During recent years polymer optical fibers (POF) have been received much attention world wide as they are expected to be useful in local area nets (LAN) used for optical communications.[1,2] Compared with silica glass optical fibers, POF have many advantages for using in LAN, such as good ductility, light weight, low melting temperature, low cost, large core diameter, and high numerical aperture, etc. In particular, a large core diameter (such as 0.5 mm or more) makes POF better transmitting media in LAN because there would be lots of junctions and connections in such short distance communications and a fine core of silica optical fibers will cause much difficulty and high cost when applications of them are made. However, all commercially available POF have been step index (SI) ones whose bandwidth of transmission is limited to about 5 MHz·km due to modal dispersion.[3] The narrow bandwidth of SI POF has confined the use of POF only to light guides and illumination components so far.

It has been known that with graded index (GI) fibers 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 bandwidth can be maximized by optimizing the shape of the graded index distribution of the fiber core. The index distribution is often expressed by a power law of a form

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

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 is the radius of the fiber core. The bandwidth is maximized when g is about 2 according to the theoretical analysis.[5] However, the limits of bandwidth which are theoretically possible with an optimum refractive index distribution are difficult to achieve for a silica optical fiber in practice. Single-mode SI silica optical fibers have been developed in past years and widely used as long-distance and high-speed communication media, although there are difficulties in handling, jointing, and fabrication for a small core of the single-mode fibers.[4]

Stimulated by the above practical and theoretical considerations, technology has been developed for preparing a graded index polymer optical fiber (GI POF) which has a parabolic profile of refractive index on the cross section of the fiber. Interfacial-gel polymerization[6] is often used to obtain the refractive index profile along with many other methods.[7−12] Generally speaking, there are two steps for preparing GI POF by the method of interfacial-gel polymerization: the first is the preparation of preforms, and the second is the drawing of a 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 distribution of a doped molecule, which is formed by the doped molecule diffusing into a gel phase on the inner wall of the polymerization container, since the refractive index of the dopant is higher than that of polymer. Although the interfacial-gel polymerization method is very simple in principle and the reproducibility of the refractive index distribution has been confirmed in several systems, the distribution of the dopant in the interfacial-gel polymerization has not been found to be dealt with theoretically. In this paper a graded index poly(methyl methacrylate) preform is made by a interfacial-gel polymerization and a model given in terms of diffusion theory of polymer-solvent system is applied in predicting the GI profile of preforms made from methyl methacrylate (MMA) and bromobenzene (BB). The model is compared with experimental results.

Theory

The free volume theory can be assumed to be valid when there is a sufficient amount of polymer−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.[13] In a general version of the free volume theory of self-diffusion, 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

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sufficient size so that the diffusing molecule can jump. The second probability is of course concerned with the availability of sufficient hole free volume for transport to occur. It has generally assumed that the diffusion process is free volume driven for temperature sufficiently close to the glass transition temperature of the system.[14] 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.[15] This means that the diffusion in bulk system above and close to the glass temperature is the same as the diffusion in the polymerization system below and close to the limiting conversion. In other words, the higher is the conversion, the smaller is the free volume drive. Furthermore, it can be expected that diffusing molecules, if there are, will distribute according to the conversion gradient, if it exists, in a closed system and the distribution of diffusing molecules will be kept afterward as the polymerization continues. The distribution of diffusing molecules can be predicted by the distribution of their diffusion coefficients along the conversion gradient. Consequently, the usual attention has been focused on the self diffusion coefficient of the diffusing molecule, D_1, which can be determined using the following expressions for a polymer-dopant mixture: [16]

$$\ln D_1 = \ln D_0 - \frac{E}{RT} - \left[\frac{(1-\omega)\hat{V}_1^* + \omega\xi\hat{V}_2^*}{\hat{V}_{\mathrm{FH}}/\gamma}\right] \quad (2)$$

$$\hat{V}_{\mathrm{FH}}/\gamma = (1-\omega)\left(\frac{K_{11}}{\gamma}\right)(K_{21} + T - T_{\mathrm{g1}}) + \omega\left(\frac{K_{12}}{\gamma}\right)[K_{22} + \alpha(T - T_{\mathrm{g2}})] \quad (3)$$

The dopant, which is used in this paper instead of penetrates or solvents in other papers, is component 1 and the polymer is component 2. Also D_0 is an effectively constant preexponential factor, E is active energy, $\hat{V}_i^*$is the specific hole free volume of component i required for a jump, ω is the the mass fraction of polymer, T is the temperature, T_{gi} is the glass transition temperature of pure component i, ξ is a size parameter which is the ratio of the critical molar volume of the small molecule jumping unit to the critical molar volume of the polymer jumping unit, $\hat{V}_{\mathrm{FH}}/\gamma$ is the solution free volume, (K_{11}/γ), K_{21}, (K_{12}/γ), and K_{22} are free volume parameters. The parameter, α, gives a zero polymer free volume at 0 °C according to the work reported previously.[16]

The above free volume formulation is based on the utilization of the following four assumptions.

(1) The partial specific volumes of the dopant and polymer are independent of composition so that no volume change on mixing.

(2) All thermal expansion coefficients are adequately represented by average values over the temperature interval of interest.

(3) The parameter γ is the same over the complete concentration interval.

(4) The energy E is the same for all dopant concentrations.

Discussions on these assumptions have been given in detail recently.[15,17,18] The procedure proposed above is of course semipredictive because at least two diffusivity data points are needed in the evaluation of the parameters in eqs 2 and 3. A predictive method for the evaluation of D_1 can be used only if it is further assumed that $E = 0$ and also that the entire dopant molecule is the dopant jumping unit.[14] These assumptions are also used in the interfacial-gel polymerization when applying the free volume theory to calculate the GI distribution on the cross section of the preform. Detailed treatments can be found in the model evaluation section. Furthermore, on the basis of these assumptions and at a given temperature, the self-diffusion coefficient can be considered as a function of polymer concentration according to eqs 2 and 3.

Experimental Section

Polymerization. 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 on 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 into a glycerin bath with a constant temperature of 80 °C for 1 h and then 70 °C until the solidification was fulfilled. 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.

Characterization. The refractive index was measured by the oil immersion method. A series matching oils were used with the Δn of two adjacent oils being 0.003. Samples were 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 refractive index was determined by the Becke-line method on a Olympus polarization microscope. The accuracy of this measurement was in the range of ±0.0015.

Evaluation of a Model for Forming a Graded Index Profile in Interfacial-Gel Polymerization

Different from other polymerization processes, interfacial-gel polymerizations are carried out in a container composed of polymers which can be dissolved into monomers 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, in which the polymer contents are between 20% and 80% in general, due to the so-called "gel effect". Therefore, the polymerization is faster in the gel phase than in the polymer content > 80% phase, which is closer to the tube inner wall, and in the polymer content < 20% phase, which is closer to the center region of the tube as the dissolvation process is a diffusion process of monomer and dopant from the center range to the wall 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 radial direction of the tube. By optimization of polymerization conditions, it has been known[6] that at a certain time the polymer phase reaches the center axis of the tube and an equilibrium state is formed, in which the dopant concentration decreases monotonically from the center axis to the periphery. After this time, the radial distribution of the dopant remains unchanging as the available hole free volume is fixed at each point on the cross section. 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.

A real polymer concentration distribution at the equilibrium along the radial direction of the tube has not been available at present as past studies on kinetics of polymerization were often limited to the low conversion and there is a distinct difference in the kinetics between the low and the high conversion. However, through numerous studies on intermediate to high conversion (i.e., beyond about 50% conversion of monomer into polymer), it is experimentally well established that the overall rate of polymerization decreases drastically with conversion.[19] Furthermore, at a given polymerization temperature, the limiting conversion for cessation of polymerization has been identified with the conversion at which the medium turned into a glass state.[15] For the polymerization of MMA, at 50 °C, the limiting conversion was found to be about 85%.[16] On the other hand, below the limiting conversion, polymerization is not controlled by diffusion of monomers; that is, the rate of monomer diffusing is faster than rate of polymerization, which results in the observation that the gel layer can quickly thicken in the center of the tube. From the analysis above it can be deduced that the polymer concentration gradually increases from the center to the inner wall of the tube, and the relationship between polymer concentration and the radial distance of the tube can be assumed as following

$$\omega = a \exp(r) + b \tag{4}$$

provided that $\omega = 0.1$ at $r = 0$ and $\omega = 0.9$ at $r = 0.9R$, where ω is the weight fraction of polymer, r is the radial distance, R is the outer radius of the tube, and a, and b are distribution constants.

In order to obtain the GI profile, another molecule inert to polymerization is mixed with the monomer before the polymerization and both are filled into the tube at the same time. As the gradient polymer concentration is shaped, the inert molecule and the monomer will be gradually distributed with a concentration gradient contrary to the polymer concentration gradient in the gel layer. This concentration distribution is formed by equilibrating between formation of polymers and diffusion of small molecules and is fixed when the gel layer reaches the center of the tube. According to the free volume theory, the diffusion coefficient of the inert molecule at different polymer concentration can be calculated[16] by eqs 2 and 3. Combining these with eq 4, we can obtain the relationship between the diffusion coefficient and radial distance.

As stated above, the assumptions on which the free volume theory is based are also used in the interfacial-gel polymerization when applying the free volume theory to calculate the graded index distribution. In the interfacial-gel polymerization system, two dopants, the inert molecule and the monomer, are considered. When the concentration gradient of two dopants is fixed, it is further assumed that any one of the two dopants in the equilibrium state is distributed according to its diffusion coefficient, which can be calculated by eqs 2 and 3, respectively. A a ratio of diffusion coefficients of the two dopants rather than the absolute values will be used during the evaluation of the concentration gradient of the dopant. It should be noted that there had been another method reported previously to interpret self-diffusion of both diluents in a ternary system.[20] When the method is used to calculate D_1 and D_2 in this system, there are some parameters unavailable at present, such as the jumping segment molecular weight M_j and the fractional free volume f_0. On the other hand, the physical implications of the method are not unambiguous.[20] Our primary justification for the assumption is consistent with our experimental results. If then, the diffusion coefficient under a state of equilibrium is considered, the concentration distribution of the inert molecule can be expressed as follows:[21]

$$C_1 = \frac{D_1}{D_1 + D_2}(1 - \omega) \tag{5}$$

C_1 is the concentration distribution of inert molecules, D_1 and D_2 are diffusion coefficients of inert molecules and monomers, and ω is the polymer concentration gradient. From eqs 1−5, the concentration distribution of the inert molecule along with the radial direction can be obtained.

For a compatible system, the relationship between refractive index and compositions of the system can be theoretically correlated by the Lorentz and Lorenz formulation[22]

$$\frac{n^2 - 1}{n^2 + 2} = \frac{1}{V}[(R_{||_1} - R_{||_2})C_1 + R_{||_2}] \tag{6}$$

where n is the refractive index, V is the molar volume, and $R_{||_1}$ and $R_{||_2}$ 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:

$$n = \sqrt{\frac{2[(R_{||_1} - R_{||_2})C_1 + R_{||_2}] + V}{V - [(R_{||_1} - R_{||_2})C_1 + R_{||_2}]}} \tag{7}$$

It is evident that the refractive index (n) distribution as a function of radial distance can be simulated from eqs 1−7.

Results and Discussion

Interfacial-gel polymerization used in this work is a homopolymerization process in which a PMMA tube is filled with MMA monomer mixed with polymerization initiator, the chain transfer agent, and one kind of molecule inert to the polymerization. Bromobenzene (BB, $n = 1.56$) was selected as the inert molecule in our experiment. There are many kinds of molecules, such as monomers, inert molecules, initiators, etc., diffusing in the polymerization system. In fact only two molecules need to be considered when evaluating refractive index distributions of polymer preforms: one is the monomer; the other is the inert molecule. Others could be neglected as their amounts are small, often lower than 1%.[23] The mechanism of forming the radial graded index distribution is schematically shown in Figure 1. In Figure 1a, the closed and open circles signify monomer and the inert molecule, respectively. As there is a polymer concentration gradient in the gel layer and because the inert molecule has the different diffusion coefficient at the different polymer concentration along the radial direction, the distribution of the inert molecule caused by its diffusion process is shown in Figure 1b. Finally the polymer phase reaches the center axis of the tube, and the radial distribution of the inert

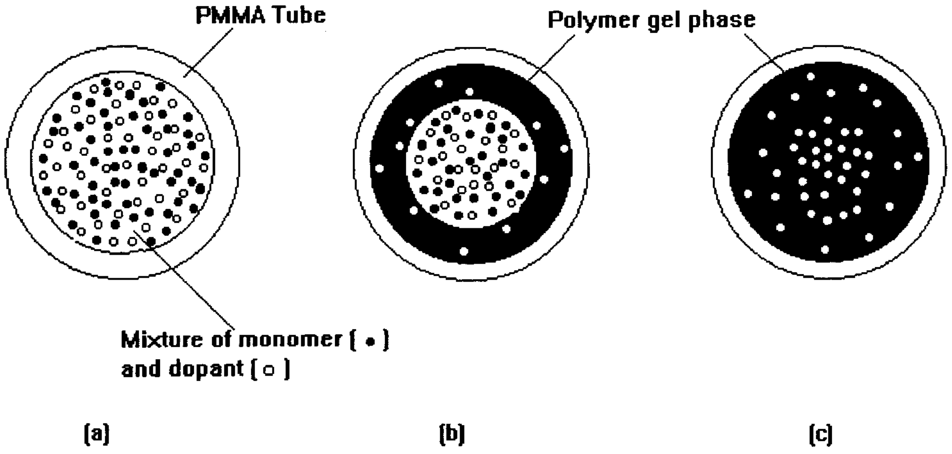

Figure 1. Schematic representation of the diffusion of dopant molecules into polymer gel phase to form the graded-index distribution on the cross section of the polymerization tube in a interfacial-gel polymerization: (a) the initial state the polymerization; (b) the period of the gel layer thickening; (c) the moment when the gel layer reaches the center of the tube.

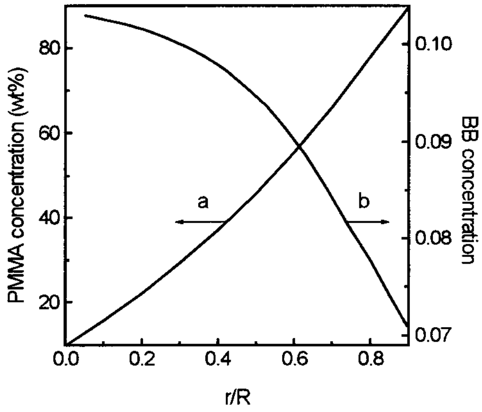

Figure 2. Values of D_{MMA} and D_{BB} as a function of PMMA concentration at 80 °C.

molecule is formed as shown in Figure 1c, in which it can be seen that the inert molecules were distributed with a gradient concentration along the direction of the radius contrary to that of polymers in the gel which is described by eq 4 and shown in Figure 2a quantitatively.

Generally speaking, to form the graded index distribution the inert molecule has to satisfy two conditions: a higher refractive index and the same compatibility to PMMA as that of MMA. BB has a higher refractive index (1.56) than that of MMA (1.42) and PMMA (1.49).[2] We found that the two chemicals can mix at any concentrations and the molecular sizes for BB and MMA are approximately the same (d = 6.9 Å) according to a calculation in terms of their densities. It has been also reported that the calculated solubility parameters are 7.814, 8.468, and 9.327 (cal/cm^3)$^{1/2}$ for MMA, BB, and PMMA, respectively.[6] When the gel layer formed, a gradient PMMA concentration existed at the vertical direction of the gel layer, which resulted from a mutual diffusion process of PMMA and the mixture solvents. At the same time, a gradient BB concentration also formed in the same direction. Because of the gel effect, which results in a higher rate of gel layer thickening than the rate of the full solidification of the layer, the gel phase would reach the center of the tube with a gradient distribution of PMMA concentration on the cross section of the tube before the gel is fully solidified. At this time, a diffusion equilibrium between PMMA and small molecules is reached and the equilibrium state can be described by the free volume theory.

The dependence of D_1 on ω can be determined eqs 2 and 3 above, if the following parameters are available:

Table 1. Vrentas–Duda Free Volume Parameters

	MMA	ref	BB	ref
$\hat{V}_1^*$ (cm^3/g)	0.87	24	0.591	25
$\hat{V}_2^*$ (cm^3/g)	0.757	24 and 27	0.757	25
$(K_{11}/\gamma) \times 10^3$ (cm^3/g·K)	0.815	26	0.64	*a*
K_{21}(K)	143	26	184.6	*a*
$(K_{12}/\gamma) \times 10^3$ (cm^3/g·K)	0.477	*b*	0.477	*a*
K_{22} (K)	52.38	*b*	52.38	*a*
T_{g1} (K)	225	29	242.4	25
T_{g2} (K)	378	23	378	23
α	0.44	16	0.44	16
D_0 (cm^2/s)	4.07×10^{-5}	*a*	1.92×10^{-5}	*a*
E (cal/mol)	0	14	0	14
ξ	0.60	16	0.60	16

[a] Calculated from the temperature dependence of MMA viscosity in ref 24 and BB viscosity in ref 25. [b] From the WLF constants in ref 28.

$\hat{V}_1^*$, $\hat{V}_2^*$, K_{11}/γ, K_{21}, K_{12}/γ, K_{22}, T_{g1}, T_{g2}, α, D_0, E, and ξ. The detailed procedure for evaluation of those parameters is given in ref 17. Fortunately, the diffusion of methyl methacrylate (MMA) in the MMA/PMMA system has been studied and the parameters of PMMA and MMA were given in previous works. The parameters needed for the evaluation of D_{MMA} are presented in Table 1 in which three free volume parameters of BB, D_0, K_{11}/γ, $K_{12} - T_{g1}$, and D_0 of MMA are calculated using viscosity–temperature and density–temperature data for BB and MMA, respectively.

Using the data listed in Table 1, the dependence of D_{MMA} and D_{BB} on polymer concentration at 80 °C was calculated by eqs 2 and 3. The result is illustrated in Figure 3. It has been verified that D is independent of PMMA molecular weight,[16] so the D_{MMA} and D_{BB} values displayed in Figure 3 include the data for all PMMA molecular weight. Also since the PMMA concentration at which the solution becomes glassy was estimated as 93% at 80 °C,[16] the free volume model, in the form of eqs 2 and 3, is valid within the concentration range adopted in Figure 3. The result in Figure 3 shows that the changing trends of D_{MMA} and D_{BB} values with PMMA concentration are identical and that D_{MMA} is slightly larger than D_{BB}, which comes mainly from the difference of correspondent D_0 values list in Table 1 calculated from MMA and BB viscosity.

The concentration distribution of BB in the radial direction can be obtained by combining the result shown in Figure 3 with eq 5 (see Figure 2b). Different from the polymer concentration distribution illustrated in Figure 2a, the concentration of BB gradually decreases

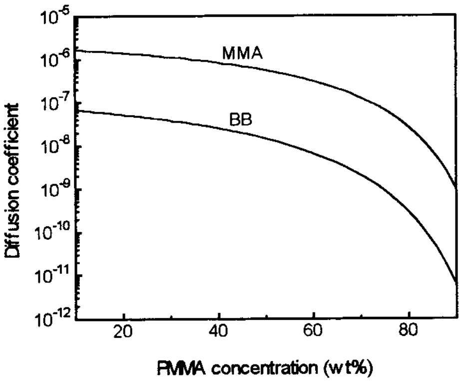

Figure 3. Radial distribution of BB concentration (a) and polymer concentration (b).

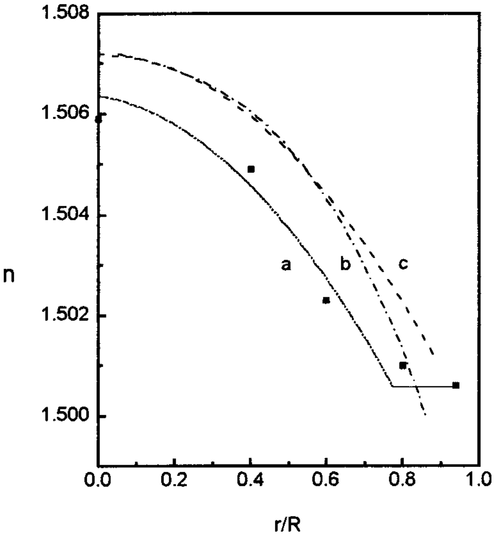

Figure 4. Refractive index distribution of PMMA preform: (a) solid curve (—) for interfacial-gel polymerization of MMA and dopant BB at 80 °C; (b) dotted curve (···) for theoretical simulation; (c) dashed curve (- - -) for calculated results by eq 1.

from the center to the periphery of the tube. Nearly at the halfway of the radius a sensible change in the rate of the decreasing can be found in Figure 2b. This is identical with experimental results found before that the overall rate of polymerization would decrease drastically with conversion increasing within a high conversion range as the diffusion is more difficult than that in a low conversion range.[19]

On the other hand, if this result is combined with eq 7 and the data $R_{\parallel_1} = 34.407$ cm^3/mol, $R_{\parallel_2} = 24.754$ cm^3/mol, and $V = 86.5$ cm^3/mol calculated in terms of the method reported before,[22] a predictive refractive index distribution can be obtained and is shown in Figure 4b. Compared with the experimental result shown in Figure 4a, the agreement between simulated and experimental curves is rather satisfactory, especially considering the fact that the practical interfacial-gel polymerization system is more complicated than the predictive model adopted in this work. From the result shown in Figure 4a, it can be seen that the preform rod has a parabolic profile of refractive index with the highest refractive index value at the center of the rod and the lowest at the periphery, which is called a cladding region and comes from the PMMA tube. The result of Figure 4a also shows that the swollen time is suitable at given PMMA tube and temperature because we had found that the PMMA tube was deformed when the swelling time was too long.

It is well-known that the bandwidth, an important parameter for GI POF, can be maximized by optimizing the shape of the graded index distribution of the fiber core.[4] When the index distribution is expressed by a power law of the form in eq 1, the bandwidth is maximized[5] when

$$g = g_{\mathrm{opt}} = 2 + \epsilon - \delta\frac{(4+\epsilon)(3+\epsilon)}{5+2\epsilon} \qquad (8)$$

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

where ϵ is the parameter of the material dispersion and n_0 and n_1 are the refractive indices of the core center and cladding, respectively. Without the material dispersion, it can be simplified as follows:[5]

$$g_{\mathrm{opt}} = 2 - \frac{12}{5}\delta \qquad (10)$$

Since δ is 0.005 for the preform in this simulation and it has been confirmed that the gradient refractive index profiles can be maintained throughout the fiber fabrication process,[6] the maximum bandwidth could be achieved when g is about 2. The index distribution expressed by the power law is calculated using the data in this work; that is, $n_1 = 1.5072$, $\delta = 0.005$, and $g = 2$. Figure 4 shows both refractive index distributions from the predictive simulation (Figure 4b) and the power law (Figure 4c), from which a similar distribution can be also found with only a little dispersion in the periphery part of the tube. It is easily deduced from the results shown in Figure 4 that GI preforms, and then GI POF, with a high bandwidth can be prepared by the interfacial-gel polymerization method.

Conclusion

A preform with a gradient refractive index distribution on its cross section has been made by a novel interfacial-gel polymerization. The distribution is considered to be formed when an equilibrium has been reached between polymerization and diffusion of inert molecules when the gel layer thickened to the center of the preform. After this time the inert molecules would be fixed in the preform because the free volume drive will stay at zero until the preform solidifies. The distribution is also calculated in terms of the free volume theory's application in a high conversion polymerization system. Analysis on the results of this work has shown that the interfacial-gel polymerization method is suitable for preparing gradient refractive index polymer optical fibers with maximum bandwidth.

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References and Notes

(1) Emslie, C. *J. Mater. Sci.* **1988**, *23*, 2281.
(2) Ishigure, T.; Nihei, E.; Koike, Y. *Appl. Opt.* **1994**, *33*, 4261.
(3) Meier, J.; Lieber, W.; Heinlein, W.; Groh, W. *Electron. Lett.* **1987**, *12*, 1208.

(4) Gambling, W. A.; Matsumura, H. *Fiber and Integrated Optics*; Ostrowsky, D. B., Eds.; Plenum Press, New York, 1978, p 333.
(5) Olshansky, R.; Keck, D. B. *Appl. Opt.* **1976**, *15*, 483.
(6) Koike, Y.; Ishigure, T.; Nihei, E. *J. Lightwave Technol.* **1995**, *13*, 1475.
(7) Ohtsuka, Y. *Appl. Phys. Lett.* **1973**, *23*, 247.
(8) Ohtsuka, Y.; Nakamoto, I. *Appl. Phys. Lett.* **1976**, *29*, 559.
(9) Hamblen, D. P. U. S. Patent 4,022,855, 1997.
(10) Koike, Y.; Nihei, E.; Tanio, N.; Ohtsuka, Y. *Appl. Opt.* **1990**, *29*, 2686.
(11) Yamatomo, T.; Mishina, Y.; Oda, M. U. S. Patent 4,852,982, 1989.
(12) Ho, B. C.; Chen, J. H.; Chen, W. C.; Chang, Y. H.; Yang, S. Y.; Chen, J. J.; Tseng, T. W. *Polym. Int.* **1995**, *27*, 310.
(13) Vrentas, J. S.; Duda, J. L. *J. Polym. Sci., Polym. Phys. Ed.* **1977**, *15*, 403, 417.
(14) Vrentas, J. S.; Vrentas, C. M. *Macromolecules* **1993**, *26*, 1277.
(15) Horie, K.; Mita, I.; Kambe, H. *J. Polym. Sci., Part A-1* **1968**, *6*, 2663.
(16) Faldi, A.; Tirrell, M.; Lodge, T. P. *Macromolecules* **1994**, *27*, 4184.
(17) Vrentas, J. S.; Vrentas, C. M. *Macromolecules* **1994**, *27*, 4684.
(18) Vrentas, J. S.; Vrentas, C. M. *Macromolecules* **1994**, *27*, 5570.
(19) *Comprehensive Chemical Kinetics*; Bamford, C. H., Tipper, C. F. H., Eds.; Elsevier: Amsterdam, 1976; Vol. 14A.
(20) Ferguson, R. D.; Von Meerwall, E. *J. Polym. Sci., Polym. Phys. Ed.* **1980**, *18*, 1285.
(21) *Physical Chemistry*; Field, V., Hameka, H. F., Blukis, U., Eds.; Macmillam Publishing Co., Inc.: New York, 1977.
(22) Van Krevelen, D. W. *Properties of Polymers*, 3rd ed.; Elsevier: New York, 1990; p 291.
(23) Zhang, Q.; Wang, P.; Zhai, Y. *J. Appl. Polym. Sci.*, in press.
(24) Haward, R. N. *J. Macromol. Sci., Rev. Macromol. Chem.* **1970**, *C4*, 191.
(25) Timmermans, J. *Physico-Chemical Constants of Pure Organic Compounds*; Elsevier: New York, 1950; p 286.
(26) Stickler, M.; Panke, D.; Wunderlich, W. *Makromol. Chem.* **1987**, *188*, 2651.
(27) Rogers, S. S.; Mandelkern, L. *J. Phys. Chem.* **1957**, *61*, 985.
(28) Ehlich, D.; Sillescu, H. *Macromolecules* **1990**, *23*, 1600.
(29) Chapiro, A. *Eur. Polym. J.-Suppl.* **1969**, 43.

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