

Preparation and Simulation of Graded-Index Polymer Rods by Interfacial-Gel Polymerization

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ABSTRACT: A graded-index (GI) polymer rod was prepared by interfacial-gel polymerization, in which polymerization was performed in a PMMA tube and bromobenzene (BB) was used as a higher refractive index molecules. By using the new technology, a GI polymer rod without any defect of void or bubble was made. A detailed mechanism and simulation of graded-index formation were given according to the Vrentas-Duda free volume theory. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 82: 3387–3390, 2001

Key words: graded-index; polymer rod; interfacial-gel polymerization; simulation

INTRODUCTION

Graded-index (GI) polymers have recently attracted extensive attention in light of their highly promising potential in optical fiber communication and polymer-based optic integrated circuits.^{1–3} The GI polymer rod is a cylindrical medium with a parabolic refractive index distribution in which the refractive index is the highest at the rod's optical axis and decreases toward the periphery with the square of the radial distance from the optical axis. The refractive index at any distance from the optical axis is given by²

$$n(r) = n_0(1 - Ar^2/2) \quad (1)$$

where $n(r)$ is the refractive index at any distance r , n_0 is the refractive index at the optical axis, A

is the positive gradient constant, and r is the radial distance from the optical axis.

Several synthetic methods have been used to prepare GI polymer rods. In this study, the interfacial-gel polymerization method was used because of the advantage of monolithic fabrication over other methods.^{3–7}

S. Y. Yang et al.³ found that increasing the concentration of the initiator from 0.5 to 1.0 wt %, and the chain-transfer agent from 0 to 1000 ppm could reduce the defect of GI polymer rod because shrinkage of the polymers is reduced by decreasing the molar weight of the prepared polymer. But increasing of concentration of initiator or chain transfer would lead to increasing of the impurity and optical attenuation of the GI polymer rods.

Jui-Hsiang et al.² found that interfacial-gel polymerization forming voids and bubbles was the result of the gel effect of polymerization. To avoid the drawbacks of the method, they proposed a new method, the swollen gel polymerization technique, for preparing the GI polymer rod. Using this method, a monomer solution was filled in the PMMA tube and the swollen gel extended from the inner wall of the PMMA tube to the center

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and the GI profile formed. After complete polymerization, a GI polymer rod without any defect of void or bubble was prepared.

This article studies the effects of reaction conditions (i.e., reaction temperature and atmosphere pressure) on the formation of voids or bubbles of the GI polymer rods. Using the Vrentas-Duda free volume model, the formation of GI profile of GI polymer rod was then simulated.

EXPERIMENTAL

Materials

Methyl methacrylate (MMA), bromobenzene (BB), benzoyl peroxide (BPO), and *n*-Dodec mercaptan (*n*-DM) were used with further purification. The length of PMMA tubes is 10.0 cm; the outside and inside diameters are 8.0 mm and 5.0 mm, respectively.

Preparation of GI Polymer Rods

The GI polymer rod was performed by interfacial-gel polymerization. One end of the PMMA tube was sealed with a silicon-rubber stopper. The monomer mixture contains 5 mL of MMA, 1 mL of BB, and 0.5 wt % of BPO, 0.1 wt % of *n*-DM. The mixture was then polymerized in PMMA tube at some temperature for 24 h, then postpolymerized at 110°C for 3 h under vacuum.

MMA was selected as an M_1 monomer with a low refractive index and BB as an M_2 monomer with a high refractive index.

First, the inner wall of the PMMA tube was swollen slightly toward to the reaction mixture; a gel phase then formed on the inner wall of the tube. Because the rate of the polymerization reaction in the gel is much faster than that in the monomer liquid phase because of the gel effect, the polymerization occurred mainly from the inner wall of the tube. M_1 monomer could more easily diffuse into the gel phase than the M_2 monomer, as first concentration of M_1 was higher than that of M_2 , and the molecular volume of M_1 is the same as that of M_2 .

When the polymer phase thickened, the concentration of the M_2 molecules in the monomer liquid phase gradually increased at the center region of the tube and concentration of M_2 in the gel phase at the center region increased. Last, the polymer phase reached the center axis of the PMMA tube and a GI polymer rod was obtained.

RESULTS AND DISCUSSION

Effects of Reaction Temperature

The effects of reaction temperature were observed as that, the more voids or bubbles of GI polymer rods were formed when higher reaction temperature. When the reaction temperature was less than 60°C, the PMMA tube was out of shape.

We considered that there were two reasons for forming voids or bubbles in GI polymer rod. First, the air dissolving in the reaction mixture and the carbon dioxide gas produced by initiator decomposing are continuously overflowing from the reaction mixture with heating. But when polymerization was carrying to some extent the average molar weight and viscosity of the reaction mixture increasing, the air and carbon dioxide could not overflow from the reaction mixture successfully, so the voids and bubbles in GI rod were then formed. Second, the rapid polymerization of the reaction mixture resulted in a high molecular weight and led to shrinkage of polymer; voids and bubbles were formed in the rod. The experimental results revealed that the GI polymer rods prepared at 60–70°C contained less void or bubble than that at higher reaction temperature and did not deform.

Effects of Reaction Atmosphere Pressure

P_0 is normal atmosphere pressure, P_1 , P_2 are the atmosphere pressure of vacuum furnace under vacuum and under high pressure, respectively. P_1 is less than P_0 , and P_2 is higher than P_0 .

We proposed that, in the former stage of reaction, when the reaction mixture was polymerized at 70°C under vacuum pressure of P_1 , the air and carbon dioxide could overflow completely from the reaction mixture; in the later stage of reaction, the reaction mixture was polymerized under high pressure of P_2 , the reaction mixture would be compressed, and the formation of the voids and bubbles led by shrinkage of polymerization was difficult. A GI polymer rod without any defect of void or bubble was prepared using the new technology, for which the refractive index profile was measured as shown in Figure 3.

THEORY AND SIMULATION

According to the Vrentas-Duda model of small molecule diffusion in polymer concentrated solu-

tions, the diffusion coefficient depends on diffusion temperature and concentrations of polymer and small molecules. The equation can be expressed as

$$\lg D_1 = \lg D_0 - \frac{E}{2.303 RT} - \frac{1}{2.303} \left\{ \frac{(1 - \omega_2)\hat{V}_1^* + \xi\omega_2\hat{V}_2^*}{\hat{V}_f/\gamma} \right\} \quad (2)$$

$$\hat{V}_f/\gamma = (1 - \omega_2)(K_{11}/\gamma)(K_{21} + T - T_{g1}) + \omega_2(K_{12}/\gamma) \times [K_{22} + \alpha(T - T_{g2})] \quad (3)$$

where the small molecule is component 1 and the polymer is component 2. D_0 is a preexponential factor; E is the activation energy; \hat{V}_i^* is the specific volumes of component i at 0 K, respectively; ξ is a size parameter; \hat{V}_f/γ is the solution free volume; K_{11}/γ , K_{21} , K_{12}/γ , and K_{22} are free-volume parameters; T is the reactive temperature; T_{g_i} is the glass-transition temperature of pure component i ; and ω_i is the mass fraction of component i . The Vrentas-Duda free volume parameters for MMA and BB are listed in Table I.

A prediction of the extended model is a linear relationship between the logarithms of the diffusion coefficients of the two small molecules:⁸

$$\lg D_{BB} = \xi_{BM} \lg D_{MMA} + \beta \quad (4)$$

where ξ_{BM} is a parameter that represents the ratio of the sizes of BB and MMA molecules, and β is the intercept. When $T \rightarrow \infty$

Table I Vrentas-Duda Free Volume Parameters

	MMA	BB
\hat{V}_1^* (cm ³ /g)	0.87	
\hat{V}_2^* (cm ³ /g)	0.757	
$(K_{11}/\gamma) \times 10^3$ (cm ³ /g · K)	0.815	
K_{21} (K)	143	
$(K_{12}/\gamma) \times 10^3$ (cm ³ /g · K)	0.477	
K_{22} (K)	52.38	
T_{g1} (K)	143	
T_{g2} (K)	378	
α	0.44	
D_0 (cm ² /s)	4.07×10^{-5}	1.92×10^{-5}
E (cal/mol)	0	
ξ	0.60	

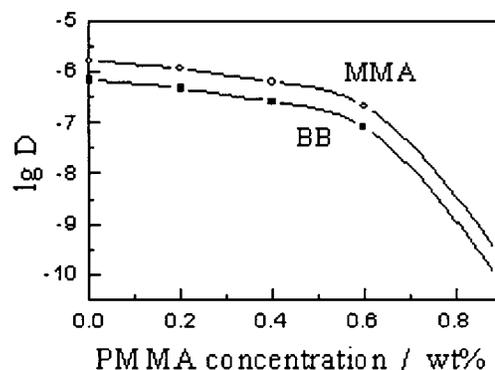


Figure 1 Values of D_{MMA} and D_{BB} as a function of PMMA concentration at 60°C.

$$\beta = \lg D_{0BB} - \xi_{BM} \lg D_{0MMA} \quad (5)$$

The dependence of D_{MMA} and D_{BB} on polymer concentration at 60°C are obtained and illustrated in Figure 1. D_{MMA} and D_{BB} are the diffusion coefficients of MMA and BB molecules.

The polymer concentration gradually increases from the center to the inner wall of the GI polymer tube. The relationship between polymer concentration and the radial distance of the tube can be assumed as follows:⁹

$$\omega_2 = a \cdot \exp(r/R') + b \quad (6)$$

where ω_2 is the weight fraction of polymer, r is the radial distance, R' is the inside radius of the tube, and a and b are distribution constants.

We deduced that, under a state of diffusion equilibrium, the concentration of the BB molecules could be expressed as follows:

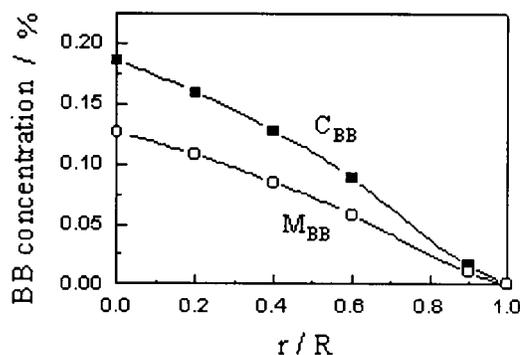


Figure 2 Radial concentration distributions of BB. C_{BB} is weight concentration; M_{BB} is mole concentration.

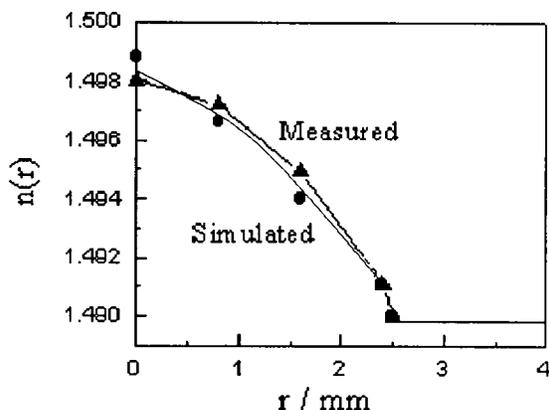


Figure 3 The measured and simulated radial refractive index distribution.

$$C_{BB} = \frac{D_{BB}\omega_{BB}}{D_{BB}\omega_{BB} + D_{MMA}\omega_{MMA}} (1 - \omega_2) \quad (7)$$

where C_{BB} is the concentration distribution of BB molecules, and ω_{MMA} and ω_{BB} are the weight fractions of MMA and BB molecules at equilibrium state. From equations (2)–(7), the weight concentration distributions of BB molecules along with the radial direction can be obtained (Fig. 2).

The mole concentration distributions of BB molecules along with the radial direction could be obtained and showed in Figure 2:

$$M_{BB} = \frac{C_{BB}}{C_{BB} + (1 - C_{BB})N_{BB}/N_{PMMA}} \quad (8)$$

where N_{BB} is the mole concentration distribution of BB, M_{BB} and M_{PMMA} are the mole weight of BB molecules, and the chain unit of PMMA polymer, respectively.

For a compatible system, according to refractive index additive theory, a relationship between $n(r)$ and M_{BB} was obtained:

$$n(r) = M_{BB}n_{BB} + (1 - M_{BB})n_{PMMA} \quad (9)$$

where $n(r)$ is system's refractive index distribution of the distance r .

When $\omega_2 = 0.1$ at $r = 0$, and $\omega_2 = 0.9$ at $r/R' = 1$, the measured and calculated $n(r)$ were showed in Figure 3. It is said the simulated curve was likely as that of measured.

CONCLUSIONS

The effects of reaction condition on the formation of defects of the GI polymer rod were investigated. By decreasing the reaction temperature, the defects of voids or bubbles of the GI polymer rod were deduced. However, too low a temperature led to deforming of the GI polymer rod. In the former stage, gas in the reaction mixture under vacuum could be easily overflowing from it. In the later stage, the reaction mixture under high pressure was compressed and the defects of voids or bubbles of the GI polymer rod were decreased. Using the new technology, a GI polymer rod without any defect of void or bubble was successfully prepared.

Using the Vrentas-Duda free volume theory, the formation of graded index profile in GI polymer rod was simulated by deducing and calculating. The result is likely as the experiments of GI polymer rod performed by the interfacial-gel polymerization.

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