

# Dielectrophoretic Technique for the Preparation of Density Gradient Polymers Doped with a Dipolar Modifier

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**Abstract:** The dielectrophoretic technique was used to prepare density gradient polymers, polystyrene doped with a dipolar modifier, diphenyl sulfide. We have measured concentration gradients of the dopant by UV/Vis spectroscopy as a function of time in a nonuniform electric field. Measured concentration data at different positions of the sample confirmed that a concentration gradient arose after a nonuniform electric field was applied to the system, these data were used to compare the concentration profile with that predicted by the dielectrophoresis equation.

**Keywords:** dielectrophoretic technique, density gradient, polystyrene with diphenyl sulfide.

## Introduction

The information technology is likely to become much more important over the 21st century. Industrial and automotive data communication cables such as data links in cars, robots and machine control, short local area networks are main application fields of plastic optical fiber (POF).<sup>1</sup> One of the most important features of POF is the possibility to adopt a large core diameter, thus allowing low installation and handling cost. It can therefore be assumed that as far as the POFs are concerned, the graded index version will be preferred type for high capacity purposes. Many researchers have extensively investigated the technology to fabricate graded index (GRIN) devices such as lens, optical fiber and so on. Koike *et al.*<sup>2</sup> demonstrated interfacial gel copolymerization techniques for steric GRIN polymer optical waveguides and lens arrays. Recently, frontal polymerization,<sup>3</sup> centrifugal diffusion polymerization,<sup>4</sup> centrifugal deposition method,<sup>5</sup> and photochemical reaction that reduces linear polarizability<sup>6</sup> were reported to prepare polymers with a desired refractive index distribution. These techniques are based on chemical modification of the organic materials, dopants or monomers and graded index profile is formed by thermal diffusion treatment.

Here we report the use of electric field to induce density gradient of the matrix polymer doped with a dipolar modifier,

more specifically the gradual decrease in concentration of the modifier from near the inner electrode to the outer electrode in a cylindrical electrode geometry. Our interest stems from the hope of using dielectrophoretic effect to develop novel approaches for the preparation of graded-index polymer optical fiber with large core diameter. During the past decade, several classes of polymeric materials that respond in a well-defined way to an applied electric field has been developed.<sup>7,8</sup> These include polymeric liquid crystals, microphase-separated block copolymers, ferro-electric polymers and second-order nonlinear optical (NLO) polymers. In previous publications<sup>9,10</sup> we reported the use of electric fields to control micropatterned domain structure of NLO side group polymers. The alignment of the side-group dipoles caused movement of adjacent backbone segments due to a nonuniform field effect, dielectrophoresis. It has been known for many years that the dielectrophoresis applies to the handling of particulate matter such as the purification and filtration of hydrocarbon oils and liquid polymers.<sup>11</sup> We investigate here transport behavior of a dipolar modifier, diphenyl sulfide (DPS) in PS matrix at high temperatures by dielectrophoretic technique.

## Experimental

Polystyrene (PS) and diphenyl sulfide (DPS, refractive index: 1.64) were used as a host material and a guest material, respectively. DPS is an agent commonly used in controlling refractive index distribution of the plastic optical fiber.

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Introduction of DPS molecules containing two benzene rings and a sulfur atom would be effective for increasing the refractive index. In this report, we focused on the measurement of the migration of the dopant molecule which is one of the important parameters in investigating the dielectrophoretic process of the dopant, and in achieving a stable refractive index profile as well. Dielectrophoretic equipment was built by using a jacketed baffled cylinder (inner radius  $r_2 = 0.4$  cm, height  $H = 20$  cm) maintained at constant temperature as schematically depicted in Figure 1. This Figure is not to scale. The PS sample was purchased from the Aldrich co. and used as received. Table I shows the physical properties of PS and DPS. A 6 kV power supply was used. The polymer (10 g) and DPS (0.1 g) were mixed in  $\text{CHCl}_3$  and precipitated into methanol. These solid flakes were then pressed to produce compact PS-DPS mixture samples. The content of DPS in PS was fixed at a rather low concentration of 1 wt% in this preliminary attempt due to phase segregation problem. The polymer mixtures has a  $T_g$  value of  $98^\circ\text{C}$  being lowered by  $4^\circ\text{C}$  due to a plasticization effect of the dopant. Prior to heating, PS-DPS mixtures were dried in a vacuum oven at  $80^\circ\text{C}$  for 48 hrs. PS-DPS mixtures were injected into the dielectrophoretic equipment at high temperature. After heating, the electric field was applied to produce final product cylinder samples. Three section of disk shape specimen cut from three cylinder samples were taken in radial direction for UV-spectroscopy.

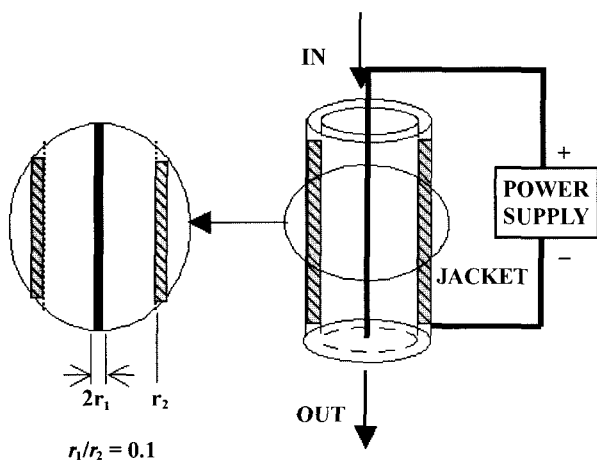


Figure 1. Schematic diagram of experimental setup.

Table I. Physical Properties of PS and DPS

	$M_w$	m.p.( $^\circ\text{C}$ )	$T_g$ ( $^\circ\text{C}$ )	Refractive Index*
PS	230,000		102	1.59
DPS	186	-40		1.64

\*Measured at the wavelength of 589.3 nm.

## Results and Discussion

We have measured the UV/Vis absorption as a function of time for a sample subjected to an electric field of 6 kV (15 kV/cm). The electric-field is limited to the value to avoid electrical breakdown. Figure 2 shows the difference in UV/Vis absorbance of specimen as a function of the radial position at the wavelength of 254.4 nm, which corresponds to the absorption maximum of DPS. The UV/Vis absorption spectra of the dopants in the PS bulk were measured near the inner electrode, middle, and periphery of the cylinder specimen subjected to the electric field at temperatures of 160, 180, and  $200^\circ\text{C}$  for 12 hrs. The absorbance changed substantially depending on the radial position of the cylinder samples. A considerable increase in concentration was observed near the center electrode whereas it decreased near the periphery of the cylinder sample. Measured concentration data at different positions of specimen confirmed that a concentration gradient arose after subjecting a nonuniform electric field to the systems. However, the concentration gradient was not evident in case of  $160^\circ\text{C}$ . This may be attributed to a short experimental time imposed on the specimen for the observation of fully developed concentration profile in this system. Apparently it seemed to take longer times than 12 hrs at this temperature for this system to attain a steady-state due to extremely slow migration of the dopants.

Furthermore, there was a significant loss in the measured DPS content due to prolonged heating in time intervals of 12 hrs which were necessary to obtain an appropriate density gradient at  $180\sim 200^\circ\text{C}$ . In fact, the total absorbances summed at three positions were revealed to be getting smaller at higher temperatures and so, a direct comparison of the absolute contents of DPS at different temperatures is not meaningful. However, this fact does not disturb the measurements of relative concentrations at different positions of the sample but leads only to small deviations in the magnitude

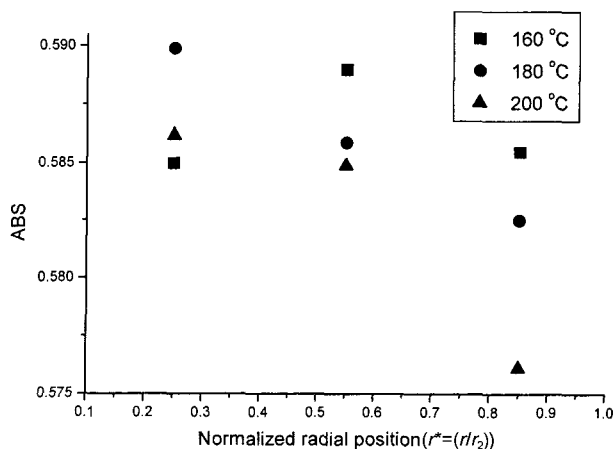


Figure 2. UV absorption at a wavelength of specimens at three radial positions under the electric field of 6 kV after 12 hrs.

of the absolute concentrations. To reduce this sublimation problem, we selected in this preliminary experiments rather low migration temperatures despite of the unrealistic processing times and we are currently preparing polystyrene copolymers containing refractive index enhancer as side groups. Another complicating feature of any study of the behavior of glassy polymers is the "aging" effects that occur with very high molecular weight samples, which lead to a progressive fall in the free volume of the melt. This aging effect complicates the interpretation of the migration data at longer times.

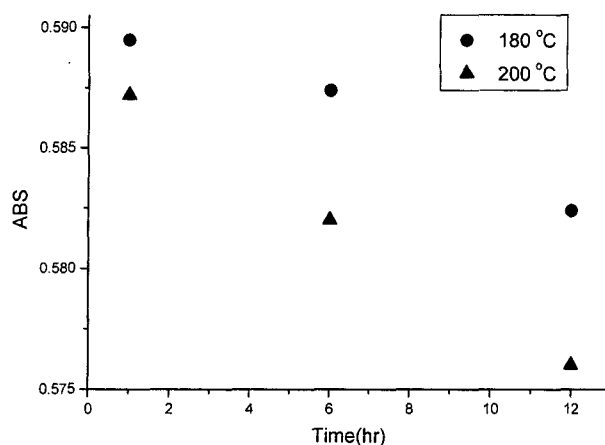
Figure 3 shows the time evolution of the UV/Vis spectra at temperatures of 180 and 200 °C near the wall of the cylinder ( $r/r_2 = 0.7 \sim 1$ ,  $r_2$ : radius of the outer electrode). The transmitted intensity decreased with time due to the dielectrophoretically created concentration gradient and the slope associated with the migration velocity increased with temperature as expected.

However, it was not possible to investigate the migration velocity quantitatively due to the limited concentration data and electric field range of experimental setup and because of the problems in DPS loss at high temperatures.

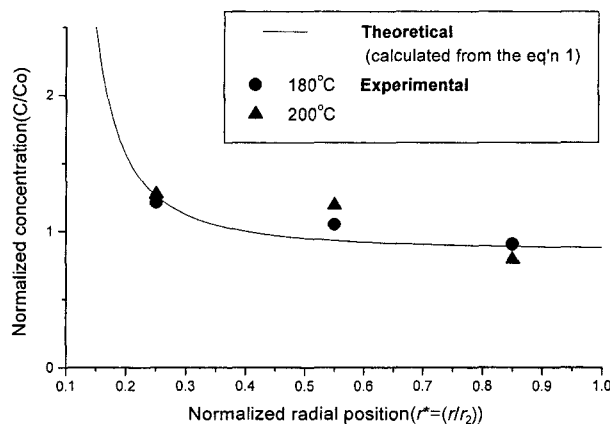
It is interesting to note also that these light intensity measurements allowed relative concentration profiles to be predicted on the same sample. We assumed that the dielectrophoretic forces are so gentle that no particles have been plated out onto the central electrode. In this case there will be a concentration gradient gradually increasing toward the central electrode. Using the following equation describing such concentration gradient after long-continued dielectrophoresis at thermal equilibrium,<sup>12</sup> we attempted to calculate a concentration profile from concentration values measured near the inner electrode, middle and periphery of the cylinder which is shown graphically in Figure 4.

$$\ln \frac{C}{C_0} = \left( \frac{z}{2D} \right) \left( \frac{1}{r^2} - \frac{1}{r_0^2} \right)$$

where  $C_0$  is the initial concentration,  $r_0$  is the position of the concentration stasis ring ( $C/C_0 = 1$ ),  $D$  is the diffusion constant and  $z$  is a constant related to the polarizability.<sup>12</sup> In order to verify if this profile could really represent the concentration distribution of the sample, we compared the experimental values with those predicted by the above equation. The experimental data marked in Figure 4 show the trend of gradual increase of concentration toward the inner electrode even if we allow for limited data of concentration measured only at three positions. This result is encouraging because it indicates that our polymer system containing dipolar molecules is electric-field responsive and a logarithmic concentration profile of the dopant molecules could be induced by long-continued application of the dielectrophoretic force. We think that the preparation of fiber sample with such a density gradient is only one step in developing optical fibers



**Figure 3.** UV absorption at a wavelength of specimens at a specified radial position of  $r/r_2 = 0.7 \sim 1$  under the electric field of 6 kV after 1, 6, 12 hrs.



**Figure 4.** Theoretical and experimental concentration distribution of DPS in PS after 12 hrs. The experimental data were normalized by using the average concentration of DPS at 12 hrs in order to compare relative concentration profiles.

and there remains much work to be done to produce a functioning materials system for the high-bandwidth and low-loss graded index plastic optical fiber.

## Conclusions

In this study, a dielectrophoretic technique was applied to the preparation of density gradient polymers doped with a dipolar modifier. The experimental materials were consisted of polystyrene and diphenyl sulfide. We have measured dielectrophoretically created concentration gradients as a function of time in electric field at temperatures 180 and 200 °C and predicted theoretically the concentration profile. Measured concentration data at different positions of the sample confirmed that a concentration gradient arose after

the application of a nonuniform electric field to the system and these data were used to compare the concentration profile with that predicted by the dielectrophoresis equation. In mild condition of dielectrophoretic process, predicted and observed values agreed at least qualitatively providing further evidence for dielectrophoretic technique suitable for the preparation of density gradient polymers doped with a dipolar modifier.

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