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Effects of para-fluorine substituent of polystyrene on gradient-index fiber-optic properties

Kotaro Koike *, Akifumi Suzuki, Kenji Makino, Yasuhiro Koike *

Keio Photonics Research Institute, Keio University, E, 7-1 Shinkawasaki, Saiwai-ku, Kawasaki, Kanagawa 212-0032, Japan

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ABSTRACT

To study the effects of fluorine substituent of polystyrene (PSt) on gradient-index fiber-optic properties, a poly(para-fluorostyrene) (P(p-FSt))-based graded-index plastic optical fiber (GI POF) is fabricated, and its properties are compared with those of a PSt-based GI POF. The para-fluorine substitution positively affects the glass transition temperature (T_g) of the core, wavelength dispersion of the optimum refractive index profile, bandwidth, and attenuation. The core T_g of the P(p-FSt)-based GI POF is 88 °C, which is higher than that of the PSt-based GI POF by 9 °C when both fibers have an identical numerical aperture (NA = 0.2). The optimum refractive index profile coefficient for the P(p-FSt)-based GI POF varies from 2.2 to 2.1 in the 600–800 nm range, whereas that for the PSt-based GI POF varies from 2.6 to 2.3 in the same wavelength region. The bandwidth of the P(p-FSt)-based GI POF is intrinsically higher than that of PSt-based GI POF. Moreover, the fiber attenuation of the P(p-FSt)-based GI POF was significantly smaller than that of the PSt-based GI POF over the source wavelength range. Our study demonstrates that P(p-FSt) has favorable properties as a GI POF base material.

1. Introduction

Polystyrene (PSt) possesses a variety of attractive qualities, such as excellent optical clarity, high thermal and chemical resistances, light unit weight, plasticity, and low manufacturing cost, making it one of the most widely used polymer resins for all uses. Unsurprisingly, PSt derivatives also have been of great interest. In particular, there have been a considerable number of studies regarding the effects of phenyl ring substitutions on the various properties of PSt, including the substituent effects on polymerization kinetics [1–6], crystallinity [7–9], solution properties [10–12], photostability [13,14], and thermal properties [15,16].

In terms of the substitution effects on optical properties, we have recently reported the effects of fluorine substituents of PSt on the polymer transparency; in particular, we have focused on the absorption of light due to the molecular vibration of carbon–hydrogen bonds [17], which is the dominant loss mechanism in most plastic optical fibers (POFs) based on amorphous optical polymers [18]. We measured the transmittance of poly(p-fluorostyrene) (P(p-FSt)), poly(pentafluorostyrene), and poly(2-trifluoromethyl styrene) at visible to near-IR wavelengths and compared the absorption wavelengths and intensities of the C–H vibrations with those of PSt [17]. As a result, we experimentally demonstrated that fluorine substitutions shift the absorption wavelengths of C–H bonds toward shorter wavelengths and decrease the absorption intensity per C–H bond because of the electron-withdrawing effect of fluorine substituents.

Here, we investigate the feasibility of P(p-FSt) as the base material of a graded-index (GI) POF, which is a highly competitive transmission medium for short-range communications such as local area networks and interconnections [19]. In general, GI POFs are characterized by their parabolic refractive index profiles in the core region, which minimizes the modal dispersion and enables high-speed data transmission over 1 Gbps. We have previously succeeded in fabricating GI POFs with PSt as the base polymer material and reported the fiber properties [20,21]. In this study, we compare the newly developed P(p-FSt)-based GI POF with the PSt-based GI POF, and we examine the contributions of a single fluorine substituent to various properties from the perspective of GI POF applications.

2. Experimental

2.1. Materials

The p-FSt and St monomers were purchased from Hokko Chemical Industry and Wako Pure Chemical Industries, respectively. Both di-*tert*-butyl peroxide (PERBUTYL® D (PBD®)) and

* Corresponding authors.
E-mail addresses: kotarokoike@kpri.keio.ac.jp (K. Koike), koike@appi.keio.ac.jp (Y. Koike).

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tert-butyl peroxy-2-ethylhexanoate (PERBUTYL® O (PBO®)) were purchased from the NOF Corporation. Dibenzothiophene (DBT) and tetrahydrofuran (THF) were purchased from Sigma Aldrich and Kanto Chemical, respectively. All other chemicals were purchased from Wako Pure Chemical Industries. The monomers were purified by aluminum-oxide column chromatography and distillation before use, while all other chemicals were used as received.

2.2. Preparation of polymer samples

For the polymerization, we used glass ampoules with 10-mm inner diameters. The ampoules were washed with distilled water and dried in a vacuum oven prior to use. The monomer mixtures, which contained 0.2 mol% of PERBUTYL® D and DBT as the free-radical initiator and the dopant, respectively, were transferred into glass ampoules and subjected to repeated freeze–pump–thaw cycles. The ampoules were subsequently flame-sealed in vacuo. The polymerizations were carried out in an oil bath at 120 °C for 48 h. The glass ampoules were carefully broken, and the polymer rods were removed.

2.3. Fabrication of graded-index plastic optical fibers

The GI POF fabrication methods can be classified into preform and extrusion methods, and certain representative principles for obtaining the GI profiles in each process are presented in [22]. In this study, we followed the previous study on PSt-based GI POFs and employed the preform method, specifically, the rod-in-tube technique. Because the general outline of the technique is described in [22,23], only the details are presented here.

The fabrication conditions of the core rod and cladding tube are summarized in Table 1. The core rod was fabricated in the same manner as described in Section 2.2. The cladding tube was polymerized with 0.30 mol% of PBO® and 0.05 mol% of PBD® in an oven at 70 °C for the first 24 h and at 90 °C for an additional 24 h. The core rod was inserted into the cladding tube, and the tube was covered with a heat-shrinkable tube. The core rod and cladding tube were subsequently heated in an oven at 160 °C or 180 °C. During the heat treatment, the core rod and cladding tube adhered to each other; the dopant diffused into the cladding layer, forming GI profiles depending on the heat treatment time. The GI preform was removed from the heat-shrinkable tube and heat-drawn into a fiber. The heat drawing for the GI preform was carried out at 240 °C, and the fiber diameter was controlled to be 490 μm.

2.4. Characterizations

Using the polymer samples, we evaluated the refractive index and glass transition temperature (T_g). For refractive index measurements, polymer discs were obtained by cutting the cylindrical polymer rods perpendicular to the long axes. The cross-sectional surfaces were polished using a polishing machine. The refractive indexes were measured using a prism coupler (Model 2010/M, Metricon) with an accuracy of ±0.0005. The probe wavelengths were 532, 632.8, 932.1, and 1310 nm. The T_g values were determined using a differential scanning calorimeter (DSC-60, Shimadzu) at a scan rate of 10 °C/min in an air atmosphere. The T_g values were measured during the second heating scan at the midpoint of the heat capacity transition between the upper and lower points of the deviation from the extrapolated rubber and glass lines.

The refractive index profile, −3-dB bandwidth, and attenuation of the resulting fibers were evaluated by the transverse interferometric technique, time domain method, and cut-back technique, respectively. The details of the fiber characterizations are the same as those reported in our previous work [20,21].

3. Results and discussion

3.1. Refractive index and glass transition temperature of doped polymers

We first studied the refractive index of P(p-FSt) containing DBT as the dopant to determine the appropriate dopant concentration for the core rod. The dopant DBT is an organosulfur compound consisting of two benzene rings fused to a central thiophene ring. Because of its planar structure and large electron resonance, DBT has been reported to increase the refractive index of doped polymers efficiently with a minimum decrease in T_g [24]. For comparison, we also prepared DBT-doped PSt in the same manner and measured the refractive index. The variation in the refractive index with dopant concentration for doped P(p-FSt) and PSt is shown in Fig. 1(a). The refractive indices were measured over a range of dopant concentrations. To calculate the refractive index at 589 nm, the measured values were fitted to the three-term Sellmeier equation [25],

$$n^2 = 1 + \sum_{i=1}^{3} \frac{A_i \lambda^2}{\lambda^2 - B_i'} \quad (1)$$

where n is the refractive index; A_i and B_i are the coefficients; and λ is the wavelength. The refractive index of P(p-FSt) was 1.556, which was lower than that of PSt by 0.036 because of the presence of the para-fluorine substituent. The refractive indices of both doped polymers increased linearly with the dopant concentration, and the slopes for the doped P(p-FSt) and PSt were 2.91×10^{-2} and 2.52×10^{-2} mol%$^{-1}$, respectively.

To quantitatively determine the DBT concentration for the core rod, we introduced a dimensionless parameter, the numerical aperture (NA), which affects fiber properties such as coupling and bending loss. The NA parameter is determined by the difference between refractive indices of the core (n_1) and cladding (n_2) as follows:

$$\mathrm{NA} = \sqrt{n_1^2 - n_2^2} \quad (2)$$

To confine light effectively in the core layer, NA should exceed 0.2. When NA equals 0.2 for P(p-FSt) and PSt (assuming identical core and cladding base materials), the core refractive indexes (n_1) must be 1.568 and 1.605, respectively. From the linear relationships shown in Fig. 1(a), the DBT concentrations corresponding to the refractive indices of P(p-FSt) and PSt were calculated to be 4.3 and 4.6 mol%, respectively.

The variation in T_g with dopant concentration for the doped P(p-FSt) and PSt samples is presented in Fig. 1(b). For P(p-FSt), T_g is 108 °C, which is higher than that of PSt (102 °C) by 6 °C. The T_g value for the doped polymers also varied linearly with the dopant

Table 1
Fabrication conditions of the core rod and cladding tube.

	Dopant (mol%)	Initiator (mol%)	Polymerization
Core rod	DBT: 4.30	PBD®: 0.20	120 °C for 48 h in oil bath
Cladding tube	–	PBO®: 0.30, PBD®: 0.05	70 °C for 24 h in oven under rotation, 90 °C for 24 h under vacuum