8278 *Macromolecules* **2005,** *38,* 8278−8284

Isomer Structure−Optical Property Relationships for Naphthalene-Based Poly(perfluorocyclobutyl ether)s

Jieun Ghim, Hwa-Sub Shim, Bu Gon Shin, Jeong-Ho Park, Jin-Teak Hwang,[†] Chaemin Chun, Seong-Hwan Oh, Jang-Joo Kim,[‡] and Dong-Yu Kim*

Center for Frontier Materials, Department of Materials Science and Engineering, Gwangju Institute of Science and Technology (GIST), 1 Oryong-dong, Puk-gu, Gwangju 500-712, Republic of Korea

Received March 9, 2005; Revised Manuscript Received August 3, 2005

ABSTRACT: Synthesis and characterization of new naphthalene-based PFCB aryl ether polymeric isomers with 1,5-, 1,6-, 2,6-, and 2,7-linkages were described. Monomers of perfluorocyclobutane (PFCB) poly(aryl ether)s, 1,5-, 1,6-, 2,6-, and 2,7-bis(trifluorovinyloxy)naphthalene, were synthesized from dihydroxynaphthalenes in two steps and polymerized by $2\pi + 2\pi$ step-growth cyclopolymerization. The naphthalene-based PFCB polymers (PFNs) had a relatively high T_g in the range 106−144 °C and excellent thermal stability at temperatures up to 400 °C. Among PFN polymeric isomers, T_g of the 1,5-linked PFCB polymer (1,5-PFN) was 30−40 °C higher than those of the other naphthalene isomers due to its high steric hindrance around the backbone. The refractive index and birefringence of the PFN polymers in the form of spin-coated films were determined. The PFN isomeric polymers showed tunability in refractive index and the birefringence of the order of 1,5 < 1,6 < 2,6 < 2,7-PFN and 1,5 < 1,6 < 2,7 < 2,6-PFN, respectively. PFN isomers had low birefringences below 0.002 except 2,6-PFN. The lowest value in birefringence was 0.0008 of 1,5-PFN due to its highly kinked structure. Plastic optical fibers of homopolymers, 1,5- and 2,7-PFN, and copolymers, 2,7-*co*-1,5-PFN and 2,7-PFN-*co*-6F−PF, were prepared, and optical losses and windows of them were observed. The attenuation loss of PFN polymers was about 0.17−0.27 dB/cm at the wavelength of near-IR optical sources. 1,5-PFN had a lower optical loss than 2,7-PFN. The optical loss of the 2,7-*co*-1,5-PFN copolymer was effectively reduced compared with that of 2,7-PFN. The lowest optical loss polymer for PFCB POF was 2,7-PFN-*co*-6F-PF of 0.07 dB/cm at the wavelength of the optical loss window and 0.17 dB/cm at 1300 nm.

Introduction

Fluorination is an efficient method for changing physical and chemical properties of molecules because fluorine is a highly electronegative atom.[1] As a result, organo-fluorine compounds have drawn considerable attention as materials for use in organic thin film transistors (OTFT),[2] organic light-emitting diodes (OLED),[3] and photonic devices.[4] For optical communication components from a network perspective, polymer-based materials have the merit of a low cost and can be prepared using low-cost processing equipment.[5] In the polymer photonics, fluorinated polymers are considered to be especially unique materials because of their low optical loss at the telecommunication operating wavelength of the near-infrared region[4,6] and the fact that they are stable in air.[7] Fluorinated or deuterated poly(methyl methacrylate) (PMMA)[8] and polystyrene (PS)[9] have been investigated for use in plastic optical fibers (POF) and waveguides. Other types of polymers such as fluorinated polyimides,[10] fluorinated poly(aryl ether)s,[11] highly fluorinated acrylates,[12] polyphosphazenes,[13] and perfluorocyclobutane (PFCB) aryl ether polymers[14] have also been studied for use as waveguides. However, fluorinated polymer-based waveguide materials are still limited to only a few types of polymers. In addition, the isomeric effect on optical properties of polymers has not been explored for the area of polymer waveguides. Desirable optical properties of waveguide materials can be obtained via isomer structure−property relationships such as the controllability of refractive index, low birefringence, and low optical loss of polymers.

PFCB-containing polymers possess many advantages over other fluorinated polymers such as their ease of processing and their excellent thermal and mechanical properties.[15] Monomers of PFCB poly(aryl ether)s can be synthesized from di- or trihydroxyl aromatic groups in two or three steps and can be polymerized in the neat or in solution without the need for a catalyst or initiator by $2\pi + 2\pi$ step-growth cyclopolymerization.[16−19] The combination of the thermally stable naphthalene backbone with the cis- and trans-1,2-disubstituted amorphous random structure of PFCB rings would be excellent for use in polymer optical waveguide devices.[19] In addition, various PFCB polymeric isomers could be readily synthesized from different hydroxyl-containing aryl-based isomers, and therefore the properties of polymers such as thermal and optical properties would be tuned by altering the position of the PFCB rings and backbone linkage. Naphthalene-based PFCB polymers could be an excellent candidate for this study because a variety of dihydroxynaphthalene isomers are commercially available.

To investigate this isomeric effect, a series of trifluorovinyl ether containing naphthalene isomers were synthesized from 1,5-, 1,6-, 2,6-, and 2,7-dihydroxynaphthalene reagents (**1**, **2**, **3**, **4**) in two steps, followed by fluoroalkylation with 1,2-dibromotetrafluoroethane and dehalogenation. The PFCB polymeric isomers were examined with respect to the tunability of their optical properties such as refractive index and optical birefrin-

---

[†] Current address: R&D Center, e-Polymers Co., Ltd. 217-4, Hwapyung-ri, Ganam-myun, Yeoju-gun, Gyunggi-do, Korea.

[‡] Current address: School of Materials Science and Engineering, College of Engineering, Seoul National University, San 56-1, Shinrim-Dong, Kwanak-Gu, Seoul, 151-744, Korea.

* To whom correspondence should be addressed: Tel +82-62-970-2319; Fax +82-62-970-2304; e-mail kimdy@gist.ac.kr.

10.1021/ma050500i CCC: $30.25

gence for possible use in photonic component materials. For the studies of optical attenuation, plastic optical fibers (POF) were prepared using these PFCB polymers, and their optical loss values were investigated. Herein we clearly demonstrate that the isomeric structures of aromatic systems in PFCB polymers greatly affect their optical properties.

Experimental Section

Materials. 1,5-, 1,6-, 2,6-, and 2,7-dihydroxynaphthalene, sodium hydride, granular zinc, and 1,2-dibromotetrafluoroethane were purchased from Aldrich Chemical Co. and used without further purification. Dimethyl sulfoxide, acetonitrile, and diethyl ether were purchased from Oriental Chemical Industries, dried over calcium hydride, and distilled before use. Granular zinc was activated with 0.1 M hydrochloric acid, washed with ethanol and ether, and dried at 140 °C under reduced pressure for 10 h.

1,5-, 1,6-, 2,6-, or 2,7-Bis(2-bromotetrafluoroethyloxy)-naphthalene (5, 6, 7, 8). The compounds were prepared in a similar manner by modification of a literature procedure.[19] To a 500 mL, three-neck flask equipped with two addition funnels and a mechanical stirrer were added DMSO (200 mL) and sodium hydride (7.2 g, 0.3 mol). DMSO (200 mL) solution dissolved with 1,5-, 1,6-, 2,6-, or 2,7-dihydroxynaphthalene (20 g, 0.125 mol) was added to a sodium hydride solution slowly through an addition funnel. The solution was stirred at room temperature for 1 h. After evaporation of hydrogen, 1,2-dibromotetrafluoroethane (78 g, 0.3 mol) was added dropwise over 1 h through an addition funnel to the reaction mixture, the temperature of which did not exceed 30 °C using a water−ice bath. The solution was stirred for 12 h at room temperature and then heated for 10 h at 40 °C. The reaction mixture was diluted with water and extracted with diethyl ether, and the organic phase was washed three times with water and dried over $MgSO_4$. The reaction mixture was purified by silica gel chromatography using hexane. The yield of **5**, **6**, **7**, and **8** was 56, 65, 60, and 70%, respectively. **5** (1,5-linkage): ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.23$ (2H, d, $J = 5.1$ Hz), 7.50 (2H, t, $J = 4.8$ Hz, 5.1 Hz), 8.05 (2H, d, $J = 4.8$ Hz). ^{19}F NMR (282.65 MHz, $CDCl_3$): $\delta = -68.06$ (2F, t, $J = 3.11$ Hz), -83.55 (2F, t, $J = 3.11$ Hz). **6** (1,6-linkage): ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.46$ (2H, d, $J = 7.7$ Hz), 7.54 (1H, dd, $J = 8.3$ Hz, 7.7 Hz), 7.74 (1H, s), 7.80 (1H, d, $J = 7.7$ Hz), 8.20 (1H, d, $J = 8.3$ Hz). ^{19}F NMR (282.65 MHz, $CDCl_3$): $\delta = -65.23$ (2F, t, $J = 3.11$ Hz), -83.59 (2F, t, $J = 3.11$ Hz). **7** (2,6-linkage): ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.43$ (2H, d, $J = 9.0$ Hz), 7.73 (2H, s), 7.89 (2H, d, $J = 9.0$ Hz). ^{19}F NMR (282.65 MHz, $CDCl_3$): $\delta = -66.58$ (2F, t, $J = 3.11$ Hz), -83.02 (2F, t, $J = 3.11$ Hz). **8** (2,7-linkage): ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.39$ Hz (2H, d, $J = 9$ Hz), 7.67 (2H, s), 7.90 (2H, d, $J = 9$ Hz). ^{19}F NMR (282.65 MHz, $CDCl_3$): $\delta = -65.67$ (2F, t, $J = 3.11$ Hz), -83.33 (2F, t, $J = 3.11$ Hz).

1,5-, 1,6-, 2,6-, or 2,7-Bis(trifluorovinyloxy)naphthalene (9, 10, 11, 12). In a 500 mL three-neck flask equipped with a reflux condenser, 1,5- (or 1,6-, 2,6-, 2,7-)bis(2-bromotetrafluoroethyloxy)naphthalene (20 g, 0.038 mol) was added via an addition funnel to a stirred solution of activated Zn (5.5 g, 0.085 mol) and dried acetonitrile (250 mL), and it was heated at 80 °C under nitrogen for 29 h. After completion of the reaction, acetonitrile was evaporated. The residual crude product was purified by column chromatography with hexane. The yield of **9**, **10**, **11**, and **12** was 65, 62, 65, and 58%, respectively. **9** (1,5-linkage): ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.23$ (2H, d, $J = 5.1$ Hz), 7.50 (2H, dd, $J = 4.8$ Hz, 5.1 Hz), 8.05 (2H, d, $J = 4.8$ Hz). ^{19}F NMR (282.65 MHz, $CDCl_3$): $\delta = -120.19$ (1F, dd, cis-CF=CF_2, F_a), -127.04 (1F, dd, *trans*-CF=CF_2, F_b), -135.29 (1F, dd, CF=CF_2, F_c), ($J_{ab} = 72.17$, $J_{ac} = 43.60$, $J_{bc} = 82.62$). FTIR (KBr): 1838 cm^{-1} (m, CF=CF_2). **10** (1,6-linkage): ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.46$ (2H, d, $J = 7.7$ Hz), 7.54 (1H, dd, $J = 8.3$ Hz, 7.7 Hz), 7.74 (1H, s), 7.80 (1H, d, $J = 7.7$ Hz), 8.20 (1H, d, $J = 8.3$ Hz). ^{19}F NMR (282 MHz, $CDCl_3$): $\delta = -117.68$ (1F, dd, *cis*-CF=CF_2, F_a), -124.08 (1F, dd, *trans*-CF=CF_2, F_b), -132.24 (1F, dd, CF=CF_2, F_c), ($J_{ab} = 72.17$, $J_{ac} = 43.60$, $J_{bc} = 82.62$). **11** (2,6-linkage): ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.34$ (2H, d, $J = 9.0$ Hz), 7.48 (2H, s), 7.83 (2H, d, $J = 9.0$ Hz). ^{19}F NMR (282 MHz, $CDCl_3$): $\delta = -120.54$ (1F, dd, cis-CF=CF_2, F_a), -127.33 (1F, dd, *trans*-CF=CF_2, F_b), -135.34 (1F, dd, CF=CF_2, F_c), ($J_{ab} = 72.17$, $J_{ac} = 43.60$, $J_{bc} = 82.62$). **12** (2,7-linkage): ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.26$ (2H, d, $J = 9.0$ Hz), 7.43 (2H, s), 7.83 (2H, d, $J = 9.0$ Hz). ^{19}F NMR (282 MHz, $CDCl_3$): $\delta = -120.28$ (1F, dd, cis-CF=CF_2, F_a), -127.12 (1F, dd, *trans*-CF=CF_2, F_b), -135.4 (1F, dd, CF=CF_2, F_c), ($J_{ab} = 72.17$, $J_{ac} = 43.6$, $J_{bc} = 82.62$).

Table 1. Molecular Weights and Thermal Properties of Naphthalene-Based PFCB Polymers (PFNs)

polymers	T_d[a] (°C)	T_g[b] (°C)	M_n[c]	M_w	PD
1,5-PFN	412	144	26 400	68 100	2.5
1,6-PFN	443	110	46 100	298 000	6.4
2,6-PFN	473	117	45 400	372 200	8.2
2,7-PFN	474	106	38 600	263 000	6.8

[a] Temperature of 10% weight loss determined in nitrogen atmosphere to 600 °C. [b] DSC thermogram obtained with a heating rate of 10 °C/min. [c] In THF vs polystyrene.

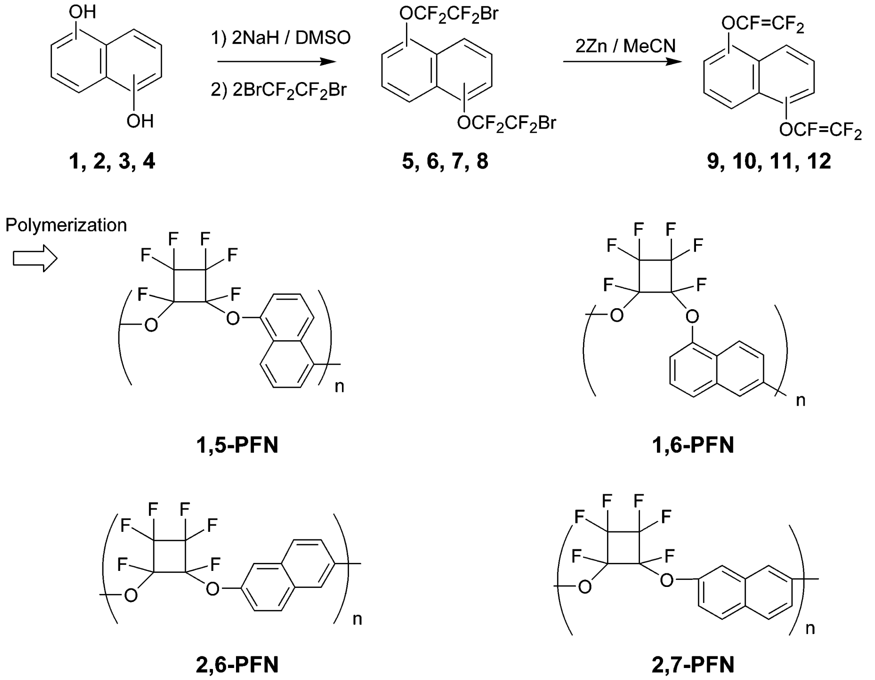
Polymerization of PFCB Monomers. PFCB monomers, distilled and degassed, were placed in a glass tube, which was sealed under high-vacuum conditions. The monomers in the sealed glass tube were bulk polymerized at 180 °C for 18 h and additionally at 200 °C for 4 h. The glass tube was then removed, leaving a transparent plastic rod, which was dried to remove unpolymerized monomers in a vacuum oven below the glass transition temperature. The PFCB ring structure in the polymers was typically characterized by multiple peaks of ^{19}F NMR in the range of −127 to −133 ppm and by FT-IR. When the monomers were polymerized, the CF=CF_2 stretching vibration peak at 1833 cm^{-1} disappeared, and new PFCB ring peaks appeared at 965 cm^{-1}. Characterizations of the polymers such as molecular weights and thermal properties are summarized in Table 1.

Refractive Index and Birefringence. Prepared PFCB polymers were dissolved in cyclohexanone at the concentration of 40 wt %. The solution was filtered with a 0.2 μm Teflon membrane syringe filter. The filtered solution was spin-coated on the silicon wafer substrate at the spin rate of 1500 rpm for 1 min. After coating the films were baked at 180 °C for 1 h. By adjusting concentration of the polymer solution, the film thickness was controlled. The thickness of the obtained films was about 5−6 μm. The refractive indices, n_{TE} and n_{TM} of the polymer films, were measured with a Sairon SPA-3000 prism coupler at 1550 nm.[20]

Plastic Optical Fiber Formation. PFCB monomers distillated and degassed to remove impurity were placed in a glass tube with the diameter of 10 mm and the length of 100 mm, which was sealed in high-vacuum conditions. The monomers in the sealed glass tube were polymerized at 180 °C for 18 h. After polymerization, the plastic rod was carefully removed from the glass tube and placed in the middle of a coiled heater and drawn at 170−180 °C, leading to plastic optical fibers with a typical diameter of 1 mm.

Optical Loss Measurement. The optical attenuation spectrum of a POF was measured by the cut-back method. The light from a tungsten lamp passed through a monochromator (Acton Research Co sp-150) controlled by computer. The emitted light from the monochromator was focused to the end surface of the PFCB fibers, connected to optical coupler. The transmitted light from the fiber was focused to the photodetector. The starting length of fiber used for the cut-back method was 30 cm. After cutting 10 cm of fiber, optical attenuation of the fiber was measured again. The optical attenuation spectrum of a POF was measured twice with the ending length of 10 cm. Optical loss of the fiber was determined by difference of optical attenuation.

Scheme 1. Synthesis and Cyclopolymerization of Naphthalene-Based Trifluorovinyl Ether Monomers



Results and Discussion

Monomer Synthesis and Cyclopolymerization. A series of trifluorovinyl ether containing monomers (**9**, **10**, **11**, **12**) were synthesized from 1,5-, 1,6-, 2,6-, and 2,7-dihydroxynaphthalene reagents (**1**, **2**, **3**, **4**) in two steps: fluoroalkylation with 1,2-dibromotetrafluoroethane and dehalogenation via zinc as shown in Scheme 1. The synthetic procedures used were similar to previously reported ones.[19] In the case of fluoroalkylation, we found that, instead of a commomly used base such as potassium hydroxide (KOH), the use of sodium hydride (NaH) was more convenient and significantly reduced the reaction time. However, the remaining hydride reagent could be highly reactive with moisture. Therefore, before the extraction procedure the reaction mixture was diluted with ice water and stirred for 30 min to prevent activation of NaH. The yields of fluoroalkylation products were 56−70%. In the dehalogenation step, we used dried zinc and solvent because moisture could reduce the activation of zinc. Granular zinc was activated with 0.1 M hydrochloric acid, washed with ethanol and ether, and dried at 140 °C under reduced pressure for 10 h. The monomers (**9**, **10**, **11**, **12**) were purified by silica gel column chromatography and then vacuum-distilled to remove moisture and impurities.

PFCB-containing polymers, PFNs, were obtained by thermal bulk polymerization via $2\pi + 2\pi$ cyclodimerization. High molecular weight and thermally stable PFN polymers could be produced. However, for desirable optical properties of PFN polymers, optimized polymerization conditions were required because severe polymerization condition leads to the development of yellow color, which can induce a large optical loss, especially at relatively short wavelengths.[19] As shown in Figure 1, the DSC thermogram of the monomer showed a melting endothermic peak and a exothermic peak near 160 °C of T_{onset} and 220 °C of T_{max}, respectively, with heat capacity values of 440−460 kcal/mol in the broad range of 160−280 °C. These exothermic peaks informed that the temperature of above 160 °C were required for the monomers to dimerize for cyclopolymerization. In the previous work (ref 19), we studied the number-average molecular weights (M_{n}) of 1,5-PFN polymer as a function of polymerization condition, and M_{n} of 1,5-PFN was 21 000 under the polymerization condition at 180 °C for 18 h. Herein, PFN monomers were polymerized at 180 °C for 18 h and then at 200 °C for an additional 4 h for improved thermal and optical properties. As shown in Table 1, M_{n} of 1,5-PFN and other polymers were 26 400 and near 40 000, respectively. Under the same polymerization conditions, the molecular weight of 1,5-PFN was lower than those of the other PFN polymers. For example, when polymerized at 160 °C for 12 h, the M_{n} for 1,5-PFN was about 4600, 3 times lower than those of the other polymers. The isomeric effect on the molecular weights of the resulting PFCB polymers is not well understood at the present time.

The PFN polymers were thermally stable at the temperatures up to 400 °C and had high glass transition temperature (T_{g}) above 100 °C, as shown in Figure 2. The combination of the rigid backbone of the naphthalene unit with the stable PFCB rings with 1,2-cis and trans mixtures led to the production of thermally stable and amorphous polymers. DSC thermograms and polarized optical microscope images revealed that all four PFN polymers showed amorphous morphology regardless of isomer types. Among the naphthalene isomers, 1,5-PFN showed the highest T_{g} of 144 °C. The T_{g} values changed, depending on the rigidity of the polymer main chain, due to the increase in the energy barrier for segmental motion. In the literature reporting poly(arylene ether)s, based on dihydroxynaphthalene isomers, the 1,5-naphthalene linkage also showed a higher T_{g} than other isomers with 2,7- and 1,4-linkages, similar to our case.[21] The 1,5-linkage appeared to hinder the mobility of segmental motion more effectively than the other isomers.

Optical Properties of Naphthalene Isomers. The refractive index (RI) could vary with polarizability of the material, packing density, temperature, humidity,

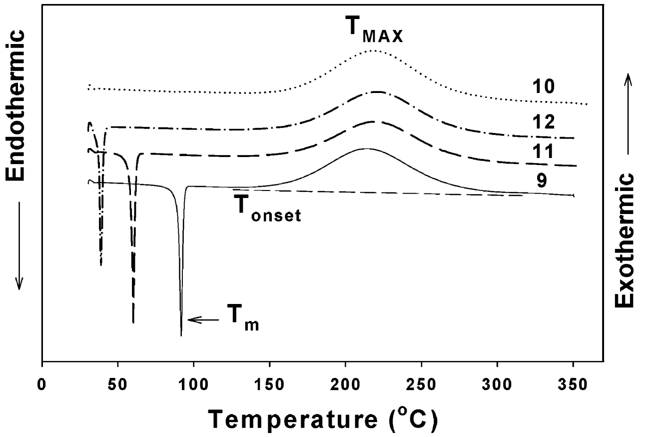


Figure 1. DSC thermograms of PFN monomers.

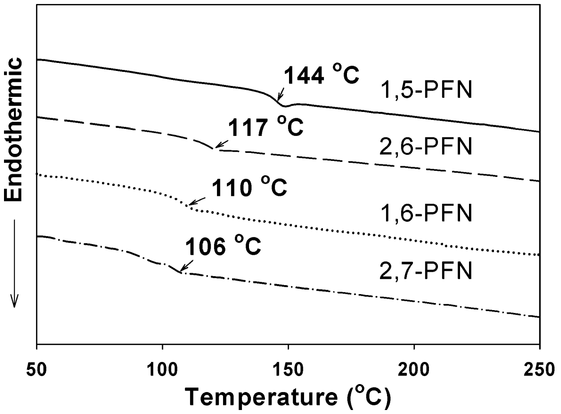


Figure 2. T_g of PFN polymers.

and birefringence, while birefringence (Δn) is mainly dependent on the anisotropy of the polymer films.[4d,f,22] Table 2 shows the RI and Δn of the spin-coated PFCB polymer films as measured by the prism-coupling method.[20] Similar to other conventional spin-coated polymer films, PFCB polymers showed a lower n_{TM} than n_{TE} because of their chain orientation in the direction parallel to the substrate during the spin-coating process. In Table 2, the TE mode RI and Δn of 1,5-PFN were 1.4962 and 0.0008, respectively, and these values were slightly different from previous reported values (n_{TE}: 1.4999; Δn: 0.0005). It is due to different M_n of 1,5-PFN. In the PFCB polymer system, a high M_n typically decreases the RI because sterically hindered perfluorocyclobutyl linkages are less polarizable than planar trifluorovinyl ether moieties and increases birefringence due to higher planarity of longer polymer chains.[14e] Copolymer of 1,5- and 2,7-PFN showed the middle value in RI and Δn of the two homopolymers. In addition, the PFN isomers showed different values each other in RI and Δn. The order of RI and Δn of those polymers was 1,5 < 1,6 < 2,6 < 2,7-PFN and 1,5 < 1,6 < 2,7 < 2,6-PFN, respectively. Previously, the tailoring of refractive index values of photonic polymer materials was studied via the copolymerization ratio,[9,10b,11c] wavelength dependence,[10b,c,11b] temperature change,[14b] or different molar fluorine ratio.[10a,11a,d] In our case, although the polymers had the same molecular formula and fluorination ratio, the PFN polymers can offer another good controllability of the RI by selecting proper isomeric structures. Different polarizability of PFCB aryl ether moieties would explain the differences in their refractive indices. Therefore, we calculated the polarizability of the basic unit of PFN polymers, 1,5-, 1,6-, 2,6-, and 2,7-bis(perfluorocyclobutyl)naphthalene ethers, in the low-energy state determined by MOPAC using the PM3 parameters of Cache 4.4.[23] As shown in Table 2, the polarizability values of PFN units were well correlated with the average refractive indices of them. A low M_n typically increases RI because trifluorovinyl groups in the chain end of polymers are more polarizable and less sterically hindered than perfluorocyclobutyl linkages.[14e] However, as discussed below, the sterically bulky and three-dimensionally more isotropic structure of 1,5-PFN would reduce the chain packing and the electronic polarizability and, as a result, reduce the refractive index compared with other isomers despite its lower M_n.

For the birefringence, 1,5-PFN showed the lowest value among all the PFN isomers. Birefringence in the spin-coated polymer film is strongly related to polymer chain orientation, among many other factors such as polymer chain rigidity, film thickness, spinning conditions, and surface energy of substrates.[24] In general, rigid aromatic groups in the polymer backbone tend to lie parallel to the substrate during the spinning process, leading to the positive birefringence with $n_{TE} > n_{TM}$. The low birefringence of 1,5-PFN, 0.0008, could be due to the orientation of the naphthalene groups normal to the polymer main chain, and also possibly normal to the substrate, due to 1,5-linkage of the backbone with naphthalene units. To confirm this hypothesis, the alignment of naphthalene backbone units in the film was investigated by s- and p-polarized UV−vis spectra (30° of the tilt angle of the incident beam). If the polymer chain is orientated in-plane or out-of-plane, s-polarized UV−vis spectroscopy shows higher or lower than p-polarization, respectively.[25] As shown in Figure 3, the difference between the s- and p-polarized absorption bands of naphthalene groups in 2,6-PFN shows the tendency of in-plane orientation of naphthalenes, while in the case of 1,5-PFN, the negligible difference between two spectra indicates a very low degree of preferential orientation of the naphthalene units. Therefore, compared with the kinked structure of the other PFN isomers, a relatively linear linkage in 2,6-PFN polymer chain seems to induce a larger birefringence. In particular, the birefringence of 1,5-PFN was considerably lower than the other isomers. As we mentioned above, 1,5-PFN had a higher T_g and the lower refractive index than the other isomers. Thus, it is evident that, as well as their thermal properties, the optical properties of PFCB polymers could be tuned simply by changing the backbone linkage of the fluorine functional group. For optical waveguide devices, low birefringence and controllability of refractive index are key requirements,[4] and from those senses, naphthalene-based PFCB polymers represent good candidates for polymer waveguide materials.

Optical Loss of PFN Polymers. PFCB polymers could be good candidates for polymer optical waveguides because of their excellent thermal, mechanical, and optical properties.[14] However, compared with other waveguide materials such as polyimides and polyacrylates, the optical loss of PFCB polymers has not been fully studied. Smith et al. and Jen et al. recently reported PFCB polymers for possible uses as polymer waveguides. The materials had the optical losses of 0.25−0.3 dB/cm at 1300−1550 nm.[14] We also previously reported a low optical loss of 0.19 dB/cm at 1300 nm for plastic optical fibers (POF) of 1,5-PFN polymer.[19]

Table 2. Optical Properties of PFN Isomers Measured at the Optical Source of 1550 nm

	refractive index				
polymers	TE mode (n_{xy})	TM mode (n_z)	n^a	polarizability^b (10^{-24} cm^2)	birefringence (Δ = TE − TM)
1,5-PFN	1.4962	1.4954	1.4959	25.148	0.0008
1,6-PFN	1.5019	1.5004	1.5014	25.324	0.0015
2,6-PFN	1.5024	1.4995	1.5014	25.329	0.0029
2,7-PFN	1.5029	1.5013	1.5023	25.783	0.0016
2,7-*co*-1,5-PFN	1.5010	1.4998	1.5006		0.0012

[a] Average refractive index, $n = (2n_{xy} + n_z)/3$. [b] Calculated values by Cache 4.4 simulation program.

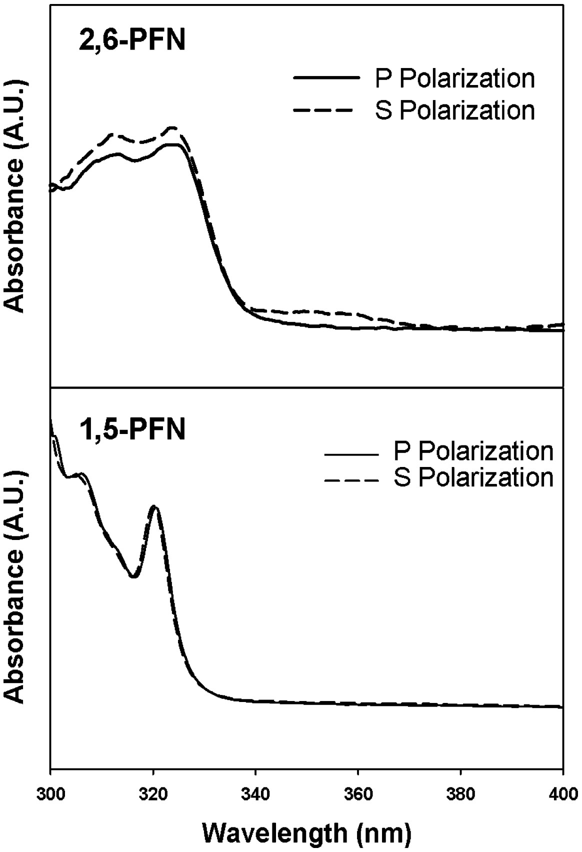


Figure 3. The s- and p-polarized UV−vis spectra of PFN polymers.

Herein we prepared using polymer waveguides 1,5-PFN to compare the difference in waveguide and fiber loss. Polymer waveguides were prepared by spin-coated films of 1,5-PFN polymer onto ZP2145 (Zenphotonics) as a cladding on 4 in. Si substrate, and the loss was measured by the prism coupling method with cut-back method, similarly with POF. Optical loss of 1,5-PFN waveguides was 0.36 dB/cm at 1550 nm at TE mode, which is higher than that of 1,5-PFN fiber. Intrinsic optical loss factors between the polymer waveguide and POF are similar. However, extrinsic loss factors between them are slightly different due to different preparation procedures. Optical loss of polymer waveguides is strongly dependent on the quality of the prepared films whereas that of POF is strongly affected by drawing conditions. The film of 1,5-PFN waveguides would contain small cracking or void; therefore, it may show higher optical loss than 1,5-PFN POF.

Table 3. Optical Loss of PFN Homo- and Copolymers at Low Loss Window and Optical Source

	optical loss (dB/cm)^a			
polymer	lowest optical loss window	1300 nm	1310 nm	1550 nm
1,5-PFN	(910 nm) 0.08	0.19	0.22	0.23
2,7-PFN	(1260 nm) 0.16	0.26	0.27	0.27
2,7-*co*-1,5-PFN (1:1)	(910 nm) 0.10	0.19	0.23	0.26
2,7-PFN-*co*-6F−PF (1:1)	(1060 nm) 0.07	0.17	0.20	0.21

[a] The error in the loss numbers was about 0.01 dB/cm.

We also examined the effect of isomeric structures of PFNs on optical loss by comparing 1,5- and 2,7-PFN and other PFCB copolymers. 2,7-PFN was selected for comparison because the polymer had a relatively low birefringence as well as a high M_n. Although a number of optical loss factors exist, such as the intrinsic loss of C−H vibrations, the main intrinsic loss factor in the near-IR region, and impurities and other extrinsic loss factors due to structure imperfections,[4d] 1,5- and 2,7-PFN might be expected to have almost similar optical loss factors because they have the same molecular formula and fluorine ratio. However, as shown in Table 3, the optical loss of 2,7-PFN was 0.03−0.07 dB/cm higher than that of 1,5-PFN over the entire wavelength range we have measured. Presumably, as discussed above, a relatively higher birefringence of 2,7-PFN than that of 1,5 PFN would have led to a higher optical loss because molecular birefringence induces anisotropic scattering loss.[4a] Rayleigh scattering related to anisotropy of polymer is proportional to the fourth power of the wavelength.[4a] The difference of optical loss between 2,7-PFN POF and 1,5-PFN POF was much higher in the short wavelength. Therefore, the factor led to the higher optical loss of 2,7-PFN could be its high birefringence. Copolymerization between 1,5- and 2,7-PFN would decrease the optical loss of PFCB POF due to the low loss and birefringence of 1,5-PFN and the high molecular weight structure of 2,7-PFN. The optical loss of the 2,7-*co*-1,5-PFN copolymer was slightly higher than that of 1,5-PFN. However, compared with 2,7-PFN, the optical loss of the copolymer was effectively reduced. Optical windows were observed at 820, 910, 1060, 1260, and 1530 nm in both cases, similar to the copolymers described below. However, 2,7-PFN showed a higher loss at 910 nm; thus, the lowest loss window was observed at 1260 nm, which is different from the case of 1,5-PFN. On the basis of the observations described above, it could be concluded that the isomeric structures also affect the optical loss characteristics, even though not as greatly as the birefringence.

We also examined copolymer of 2,7-PFN and 6F-PF to increase the amorphous morphology and fluorine ratio. The 6F-PF is a highly fluorinated PFCB polymer having good thermal and optical properties, previously reported by Smith et al.[14b] Figure 4 shows optical attenuation spectra of the PFCB polymers. The second overtone bands 3υ and the third overtone bands 4υ were in the regions of 1060−1260 and 815−910 nm, and the first combination bands $2\upsilon + \delta$ and the weak second combination bands $3\upsilon + \delta$ were in the region of 1260−1530 and 910−1060 nm, respectively. Optical windows were also observed at 820, 910, 1060, 1260, and 1530

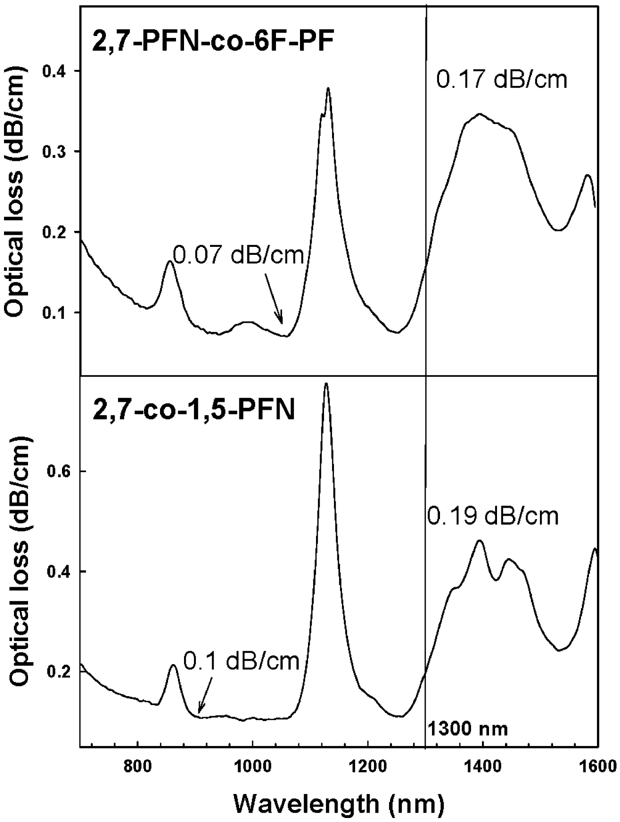


Figure 4. Optical loss spectra of PFCB copolymers in the region of 700−1600 nm.

nm. 2,7-PFN-*co*-6F−PF had the lowest optical loss among the PFCB polymers over the entire wavelength range, especially showing a very low loss of 0.07 dB/cm at the optical window of 1060 nm. This may indicate that the major factor of optical loss is the intrinsic loss due to the higher harmonics of remaining aromatic C−H vibrations because 2,7-PFN-*co*-6F-PF, which has the highest fluorine content, had the lowest optical loss among the polymers studied in this work. However, these optical loss values are still high for practical optical fiber applications compared with PMMA POFs (ca. 100 dB/Km). Several extrinsic loss factors such as monomer purity, microvoids in the fibers, and especially the lack of existing cladding could also have contributed significantly. Further substitution of hydrogens in the naphthalene groups into heavy atoms such as deuterium and fluorine would produce polymers with lower optical loss for the waveguide applications.

Conclusions

We successfully synthesized new naphthalene-based 1,5-, 1,6-, 2,6-, and 2,7-bis(trifluorovinyl ether) isomers, and the corresponding PFCB homo- and copolymers from them through $2\pi + 2\pi$ cyclopolymerization. The naphthalene-based PFCB polymers had relatively high T_g values, above 110 °C, and a high thermal stability up to temperatures of 400 °C. However, the thermal properties changed depending on the position of attachment of the PFCB rings. The T_g of 1,5-position isomer was 30−40 °C higher than those of the other naphthalene isomers. The optical properties of the PFCB polymers were investigated with respect to refractive index and birefringence as well as their optical loss as plastic optical fibers. The refractive index and the birefringence of spin-coated films of PFCB isomer polymers showed tunability with the position of attachment of the PFCB rings. The order of refractive indices and birefringence of these polymers was 1,5 < 1,6 < 2,6 < 2,7-PFN and 1,5 < 1,6 < 2,7 < 2,6-PFN, respectively. Different polarizability of PFCB aryl ether moieties would explain the differences in their refractive indices although the difference in the refractive index was not so large. 1,5-PFN films showed the lowest birefringence of 0.0008 among all the PFN isomers due to its the most kinked backbone structure. We prepared and characterized plastic optical fibers of the PFCB polymers, and optical windows were observed at 820, 910, 1025, 1260, and 1530 nm. The attenuation loss of the naphthalene-based PFCB polymers was about 0.17−0.27 dB/cm at the wavelength of the optical source in the near-IR In addition, the optical losses of those polymers were dependent on the isomeric effect of the PFCB ring; the value for the 1,5-linked PFCB polymer was lower than that for 2,7-PFN due to its higher structural anisotropy. The lowest optical loss of PFCB POF was 0.07 dB/cm at the wavelength of the optical loss window and 0.17 dB/cm at 1300 nm.

Acknowledgment. This work was financially supported by the Ministry of Science and Technology, National Research Laboratory program of KOSEF, and Heeger Center for Advanced Materials (HCAM).

Supporting Information Available: ^{1}H and ^{19}F NMR spectra of final monomer products. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) (a) Grob, U.; Rüdiger, S. T. In *Organo-Fluorine Compounds*; Baasner, B., Hagemann, H., Tatlow, J. C., Eds.; Georg Thieme Verlag Stuttgart: New York, 2000; Vol. E10a, p 18. (b) Renak, M. L.; Bartholomew, G. P.; Wang, S.; Ricatto, P. J.; Lachicotte, R. J.; Bazan, G, C. *J. Am. Chem. Soc.* **1999**, *121*, 7787.
(2) (a) Bao, Z.; Lovinger, A. J.; Brown, J. *J. Am. Chem. Soc.* **1998**, *120*, 207. (b) Facchetti, A.; Mushrush, M.; Katz, H. E.; Marks, T. J. *Adv. Mater.* **2003**, *15*, 33. (c) Sakamoto, Y.; Suzuki, T.; Kobayashi, M.; Gao, Y.; Fukai, Y.; Inoue, Y.; Sato, F.; Tokito, S. *J. Am. Chem. Soc.* **2004**, *126*, 8138.
(3) (a) Sakamoto, Y.; Suzuki, T.; Miura, A.; Fujikawa, H.; Tokito, S.; Taga, Y. *J. Am. Chem. Soc.* **2000**, *122*, 1832. (b) Heidenhain, S. B.; Sakamoto, Y.; Suzuki, T.; Miura, A.; Fujikawa, H.; Mori, T.; Tokito, S.; Taga, Y. *J. Am. Chem. Soc.* **2000**, *122*, 10240. (c) Jiang, X.; Liu, S.; Ma, H.; Jen, A. K.-Y. *Appl. Phys. Lett.* **2000**, *76*, 1813.
(4) (a) Kaino, T.; Fujiki, M.; Jinguji, K. *Rev. Electron. Commun. Lab.* **1984**, *32*, 478. (b) Resnick, P. R.; Buck, W. H. In *Modern Fluoropolymers*; Scheirs, J., Ed.; John Wiley & Sons: Chichester, UK, 1997; p 397. (c) Sugiyama, N. In *Modern Fluoropolymers*; Scheirs, J., Ed.; John Wiley & Sons: Chichester, UK, 1997; p 541. (d) Eldada, L.; Shacklette, L. W. *IEEE J. Select. Top. Quantum Electron.* **2000**, *6*, 54. (e) Tanio, N.; Koike, Y. *Polym. J.* **2000**, *32*, 43. (f) Ma, H.; Jen, A. K.-Y.; Dalton, L. R. *Adv. Mater.* **2002**, *14*, 1339.
(5) Eldada, L. *Rev. Sci. Instrum.* **2004**, *75*, 575.
(6) Groh, W. *Macromol. Chem.* **1988**, *189*, 2861.
(7) Kaino, T. *Appl. Phys. Lett.* **1986**, *48*, 757.
(8) (a) Imamura, S.; Youshimura, R.; Izawa, T. *Electron. Lett.* **1991**, *27*, 1342. (b) Yoshimura, R.; Hikita, M.; Tomaru, S.; Imamura, S. *J. Lightwave Technol.* **1998**, *16*, 1030. (c) Koo, J.-S.; Smith, P. G. R.; Williams, R. B.; Grossel, M. C.; Whitcombe, M. J. *Chem. Mater.* **2002**, *14*, 5030. (d) Kim, E.; Cho, S. Y.; Yeu, D.-M.; Shin, S.-Y. *Chem. Mater.* **2005**, *17*, 962.
(9) Pitois, C.; Wiesmann, D.; Vukmirovic, S.; Robertsson, M.; Hult, A. *Macromolecules* **1999**, *32*, 2903.
(10) (a) Matsuura, T.; Ishizawa, M.; Hasuda, Y.; Nishi, S. *Macromolecules* **1992**, *25*, 3540. (b) Matsuura, T.; Ando, S.; Sasaki, S.; Yamamoto, F. *Macromolecules* **1994**, *27*, 6665. (c) Chang, C.-C.; Chen, W.-C. *Chem. Mater.* **2002**, *14*, 4242. (d) Yen, C.-T.; Chen, W.-C. *Macromolecules* **2003**, *36*, 3315. (e)

Chang, C.-C.; Wei, K.-H.; Chang, Y.-L.; Chen, W.-C. *J. Polym. Res.* **2003**, *10*, 1.

(11) (a) Lee, H.-J.; Lee, E.-M.; Lee, M.-H.; Oh, M.-C.; Ahn, J.-H.; Han, S. G.; Kim, H. G. *J. Polym. Sci., Part A: Polym. Chem.* **1998**, *36*, 2881. (b) Pitois, C.; Weismann, D.; Lindgren, M.; Hult, A. *Adv. Mater.* **2001**, *13*, 1483. (c) Kim, J.-P.; Lee, W.-Y.; Kang, J.-W.; Kwon, S.-K.; Kim, J.-J.; Lee, J.-S. *Macromolecules* **2001**, *34*, 7817. (d) Kang, J.-W.; Kim, J.-P.; Lee, W.-Y.; Kim, J.-S.; Lee, J.-S.; Kim, J.-J. *J. Lightwave Technol.* **2001**, *19*, 872. (e) Pitois, C.; Vestberg, R.; Rodlert, M.; Malmström, E.; Hult, A.; Lindgren, M. *Opt. Mater.* **2002**, *21*, 499. (f) Li, X.-D.; Zhong, Z.-X.; Kim, J.-J.; Lee, M.-H. *Macromol. Rapid Commun.* **2004**, *25*, 1090. (g) Qi, Y.; Ding, J.; Day, M.; Jiang, J.; Callender, C. L. *Chem. Mater.* **2005**, *17*, 676.

(12) Shacklette, L. W.; Blomquist, R.; Deng, J. M.; Ferm, P. M.; Maxfield, M.; Mato, J.; Zou, H. *Adv. Funct. Mater.* **2003**, *13*, 453.

(13) Allcock, H. R.; Bender, J. D.; Chang, Y. *Chem. Mater.* **2003**, *15*, 473.

(14) (a) Fischbeck, G.; Moosburger, R.; Kostrzewa, C.; Achen, A.; Petermann, K. *Electron. Lett.* **1997**, *33*, 518. (b) Smith, D. W., Jr.; Chen, S.; Kumar, S. M.; Ballato, J.; Topping, C.; Shah, H. V.; Foulger, S. H. *Adv. Mater.* **2002**, *14*, 1585. (c) Kang, S. H.; Luo, J.; Ma, H.; Barto, R. R.; Frank, C. W.; Dalton, L. R.; Jen, A. K.-Y. *Macromolecules* **2003**, *36*, 4355. (d) Wong, S.; Ma, H.; Jen, A. K.-Y.; Barto, R.; Frank, C. W. *Macromolecules* **2003**, *36*, 8001. (e) Wong, S.; Ma, H.; Jen, A. K.-Y.; Barto, R.; Frank, C. W. *Macromolecules* **2004**, *37*, 5578. (f) Ma, H.; Luo, J.; Kang, S. H.; Wong, S.; Kang, J. W.; Jen, A. K.-Y.; Barto, R.; Frank, C. W. *Macromol. Rapid Commun.* **2004**, *25*, 1667.

(15) (a) Kennedy, A. P.; Babb, D. A.; Bremmer, J. N.; Pasztor, A. J., Jr. *J. Polym. Sci., Part A: Polym. Chem.* **1995**, *33*, 1859. (b) Liou, H.-C.; Ho, P. S.; Mckerrow, A. *J. Polym. Sci., Part B: Polym. Phys.* **1998**, *36*, 1383. (c) Choi, W.-S.; Harris, F. W. *Polymer* **2000**, *41*, 6213. (d) Smith, D. W., Jr.; Babb, D. A.; Shah, H. V.; Hoeglund, A.; Traiphol, R.; Perahia, D.; Boone, H. W.; Langhoff, C.; Radler, M. *J. Fluorine Chem.* **2000**, *104*, 109. (e) Jin, J.; Smith, D. W., Jr.; Topping, C. M.; Suresh, S.; Chen, S.; Foulger, S. H.; Rice, N.; Nebo, J.; Mojazza, B. H. *Macromolecules* **2003**, *36*, 9000.

(16) (a) Babb, D. A.; Ezzell, B. R.; Clement, K. S.; Richey, W. F.; Kennedy, A. P. *J. Polym. Sci., Part A: Polym. Chem.* **1993**, *31*, 3465. (b) Smith, D. W., Jr.; Babb, D. A. *Macromolecules* **1996**, *29*, 852. (c) Ji, J.; Narayan-Sarathy, S.; Neilson, R. H.; Oxley, J. D.; Babb, D. A.; Rondan, N. G.; Smith, D. W., Jr. *Organometallics* **1998**, *17*, 783. (d) Ma, H.; Chen, B.; Sassa, T.; Dalton, L. R.; Jen, A. K.-Y. *J. Am. Chem. Soc.* **2001**, *123*, 986. (e) Babb, D. A. In *Fluoropolymers 1*; Hougham, G., Cassidy, P. E., Johns, K., Davidson, T., Eds.; Kluwer Academic/Plenum Publishers: New York, 1999; p 25.

(17) Some PFCB monomers and intermediates are commercially available in Oakwood Co.

(18) (a) Spraul, B. K.; Suresh, S.; Glaser, S.; Perahia, D.; Ballato, J.; Smith, D. W., Jr. *J. Am. Chem. Soc.* **2004**, *126*, 12772. (b) Jin, J.; Topping, C. M.; Chen, S.; Ballato, J.; Foulger, S. H.; Smith, D. W., Jr. *J. Polym. Sci., Part A: Polym. Chem.* **2004**, *42*, 5292. (c) Smith, D. W., Jr.; Jin, J.; Shah, H. V.; Xie, Y.; DesMarteau, D. D. *Polymer* **2004**, *45*, 5755. (d) Ballato, J.; Foulger, S. H.; Smith, D. W., Jr. *J. Opt. Soc. Am. B* **2004**, *21*, 958. (e) Ligon, S. C., Jr.; Topping, C. M.; Jin, J.; Fallis, S.; Irvin, J. A.; Desmarteau, D. D.; Smith, D. W., Jr. *Macromol. Chem. Phys.* **2004**, *205*, 801.

(19) Ghim, J.; Lee, D.-S.; Shin, B. G.; Vak, D.; Kim, M.-J.; Shim, H.-S.; Kim, J.-J.; Kim, D.-Y. *Macromolecules* **2004**, *37*, 5724.

(20) Beak, S. H.; Kang, J.-W.; Li, X. L.; Lee, M.-H.; Kim, J.-J. *Opt. Lett.* **2004**, *29*, 301.

(21) Bottino, F. A.; Pasquale, G. D.; Leonardi, N.; Pollicino, A. *Polymer* **1998**, *39*, 3199.

(22) (a) Hougham, G.; Tesoro, G.; Viehbeck, A.; Chapple-Sokol, J. D. *Macromolecules* **1994**, *27*, 5964. (b) Hougham, G.; Tesoro, G.; Viehbeck, A. *Macromolecules* **1996**, *29*, 3453.

(23) Mikami, K.; Yusa, Y.; Korenaga, T. *Org. Lett.* **2002**, *4*, 1643.

(24) Ree, M.; Chu, C.-W.; Goldberg, M. J. *J. Appl. Phys.* **1994**, *75*, 1410.

(25) Servet, B.; Horowitz, G.; Ries, S.; Lagorsse, O.; Alnot, P.; Yassar, A.; Deloffre, F.; Srivastava, P.; Hajlaoui, R.; Lang, P.; Garnier, F. *Chem. Mater.* **1994**, *6*, 1809.

MA050500I