Optical Properties of Perfluorocyclobutane Aryl Ether Polymers for Polymer Photonic Devices

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ABSTRACT: New thermoplastic PFCB aryl ether monomers, 1,5-bis(trifluorovinyloxy)naphthalene (TFVON) and 1,4-bis(trifluorovinyloxy)benzene (TFVOB), were synthesized, and homopolymers, PTFVON and PTFVOB, and a copolymer, TFVON-co-TFVOB, were successfully prepared from them by $2\pi + 2\pi$ cyclopolymerization. The C-H vibrational absorption of the monomer was investigated by IR and near-IR spectrum analysis. The optical properties of the polymers in the form of plastic optical fibers and thin films were examined. The absorptions corresponding to fundamental and overtones of C-H vibrations in PFCB monomers were greatly reduced due to the presence of the fluorine substituents, which could lead to low attenuation loss of the resulting polymers in the near-IR region. Polymerization conditions such as temperature and time significantly affected the optical loss values of the polymers as well as their molecular weights and thermal properties. We prepared plastic optical fibers of the PFCB polymers, and optical windows were observed at \$20, 910, 1025, 1260, and 1530 nm. The attenuation loss of PTFVON was typically 0.083 dB/cm at 910 nm, the lowest optical window, 0.190 dB/cm at 1300 nm, and 0.227 dB/cm at 1550 nm. Copolymerization further reduced optical loss, and optical loss of the copolymer was about 0.03-0.1 dB/cm lower than that of the homopolymer. A birefringence of the spin-coated films of the PFCB polymers was also investigated and found to be exceptionally low. A birefringence of less than 0.001 was found in all the polymers. The lowest birefringence of 0.0005 was measured for PTFVON films.

Introduction

In photonic telecommunication devices, plastic optical fibers (POF) and polymer waveguides are of great interest due to their ease in processing, controllability of optical properties, and their low cost.¹⁻⁷ However, most hydrocarbon-based polymers show a large transmission loss in the visible and near-IR region due to the vibrational overtone absorption of C-H bonds. Therefore, fluorinated polymers have been investigated because they show a low optical loss.¹⁻⁶ From the point of view of low optical loss, perfluorinated polymers would be expected to show the best transmission behaviors. Teflon AF of Dupont and Cytop of Asahi Glass are typical examples of commercialized amorphous fluoropolymers that have good optical properties and show low transmission loss values.7 However, the high cost of preparation of these polymers inhibits their use in potential applications to photonic devices. In addition, the lack of controllability of optical and other properties has also prevented the widespread use of these materials. Therefore, fluorinated and deuterated poly(methyl methacrylate) (PMMA)^{6,8} and polystyrene (PS)⁹ have been investigated for use in POF and waveguides, and fluorinated polyimides,^{10–12} fluorinated poly(aryl ether)s,^{13–15} highly fluorinated acrylates,^{1,16} and perfluorocyclobutane (PFCB) aryl ether polymers¹⁷⁻²⁰ have been studied for use as waveguides.

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Among these polymers, PFCB-containing polymers possess many advantages over other fluorinated polymers such as their ease of processing and excellent thermal and mechanical properties. Monomers of perfluorocyclobutane (PFCB) poly(aryl ether)s are easily synthesized 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, resulting in conversions in excess of 99%.^{21,22} Through the insertion of various functional groups via Suzuki coupling, lithium-halogen exchange reactions, or other methods between trifluorovinyl aryl ether (TFVE) linkages,²³⁻²⁵ PFCB polymers could lead to an increased processability, durability, chemical resistance, high thermal stability, and optical properties, thus resulting in various optical materials for use as both core and cladding materials for waveguides, coatings, light-emitting diodes, liquid crystal polymers, and interlayer dielectrics. $^{26-30}$

Much attention has been paid to photonic applications of PFCB polymers. Nevertheless, our knowledge of detailed optical properties such as optical loss at various wavelengths and the birefringence of the PFCB polymers is, to some extent, limited.^{20,22}

In this study, we reported on the preparation of new PFCB polymers and two of their most important optical properties for photonic components: optical attenuation at various wavelengths and optical birefringence ($\Delta = n_{\text{TE}} - n_{\text{TM}}$). A new naphthalene-based PFCB monomer, 1,5-bis(trifluorovinyloxy)naphthalene (TFVON), was synthesized and polymerized.³¹ The naphthalene ring provides a rigid structure to the polymer and could yield a moderately high T_{g} polymer comparable to the well-known biphenyl-based PFCB polymer.²² However, compared to 1,4-disubstituted biphenyl units, 1,5-disubstituted naphthalene could show better birefringence

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characteristics because the molecular axis is perpendicular to the main backbone direction. We also prepared 1,4-bis(trifluorovinyloxy)benzene (TFVOB) and a corresponding polymer that has a higher fluorine content than PTFVON. Effects of copolymerization of these two monomers on optical properties were also investigated.

For the studies of optical attenuation, infrared (IR) and near-IR spectra of the monomers were analyzed, POFs were prepared using these PFCB polymers, and their optical loss values as a function of various polymerization conditions were investigated. From the prepared POFs, we were able to obtain full transmission loss spectra of these polymers in the near-IR region.

Experimental Section

Materials. Hydroquinone, 1,5-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 distillated 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.

Characterization of Monomers and Polymers. ¹H NMR and ¹⁹F NMR spectra were obtained with a JEOL JNM-LA 300 WB FT-NMR in chloroform-d. The chemical shifts of ¹H NMR were referenced to tetramethylsilane (TMS) at 0 ppm, and those of ¹⁹F NMR were referenced to fluorotrichloromethane (CFCl₃) at 0 ppm. IR and near-IR spectra were measured by a Perkin-Elmer IR 2000 series and Hitachi U-3501, respectively. Gel permeation chromatography (GPC) data were collected from a Waters model at 40 °C equipped with four Waters columns. Tetrahydrofuran was used as the eluent at a flow rate of 1.0 μ L/min, and polystyrene was used as the standard. The eluent was monitored with a refractive index detector. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) measurements were performed with a TA Instrument 2100 series under a nitrogen atmosphere at a heating rate of 10 °C/min.

1,5-Bis(2-bromotetrafluoroethyloxy)naphthalene. To a 1 L, three-neck flask equipped with two addition funnels and a mechanical stirrer were added DMSO (400 mL) and sodium hydride (12 g, 0.50 mol). DMSO (400 mL) solution dissolved with 1,5-dihydroxynaphthalene (40 g, 0.25 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 (130 g, 0.50 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 50 °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 MgSO₄. The reaction mixture was purified by silica gel chromatography using hexane to obtain the colorless liquid. The yield was 56%. ¹H NMR (300 MHz, CDCl₃): $\delta = 8.1$ (2H, d, J = 4.8 Hz), 7.58 (2H, t, J = 4.8 Hz, 5.1 Hz), 7.49 (2H, d, J = 5.1 Hz). ¹⁹F NMR (282.65 MHz, CDCl₃): $\delta = -83.55$ (t, J = 3.11 Hz), -68.06 (t, J = 3.11 Hz).

1,5-Bis(trifluorovinyloxy)naphthalene (TFVON). 1,5-Bis(2-bromotetrafluoroethyloxy)naphthalene (40 g, 0.077 mol) was added via an addition funnel to a stirred solution of activated Zn (12.7 g, 0.193 mol) and dried acetonitrile (400 mL) at 80 °C under nitrogen for 29 h. After completion of the reaction, acetonirile was evaporated. The residual crude product was purified by column chromatography with hexane to obtain a white solid. Melting point = 91 °C. The yield was 65%. ¹H NMR (300 MHz, CDCI₃): δ = 8.1 (2H, d, *J* = 4.8 Hz), 7.58 (2H, dd, *J* = 4.8 Hz, 5.1 Hz), 7.49 (2H, d, *J* = 5.1 Hz). ¹⁹F NMR (282.65 MHz, CDCI₃): δ = -116.9 (1F, dd, cis-CF=CF₂,

F_a), -123.60 (1F, dd, trans-CF=CF₂, F_b), -131.36 (1F, dd, CF=CF₂, F_c) (J_{ab} = 72.17, J_{ac} = 43.6, J_{bc} = 82.62). FTIR (KBr): 1838 cm⁻¹ (m, CF=CF₂).

1,4-Bis(2-bromotetrafluoroethyloxy)benzene. This compound was prepared according to the synthetic method of 1,5-bis(2-bromotetrafluoroethyloxy)naphthalene using hydroquinone (27.5 g, 0.25 mol) with sodium hydride (12 g, 0.5 mol) in DMSO (400 mL). The yield was 43%. ¹H NMR (300 MHz, CDCl₃): δ = 7.27 (4H). ¹⁹F NMR (282.65 MHz, CDCl₃): δ = -83.548 (t, *J* = 3.11 Hz), -65.80 (t, *J* = 3.11 Hz).

1,4-Bis(trifluorovinyloxy)benzene (TFVOB). This compound was prepared according to the synthetic method of 1,5bis(trifluorovinyloxy)naphthalene using 1,4-bis(2-bromotetrafluoroethyloxy)benzene in acetonitrile. The residual crude product was purified by column chromatography with hexane to obtain a colorless liquid. The yield was 54%. The synthetic method for TFVOB was also described in the patent disclosure from Dow Chemical Corp.³² ¹H NMR (300 MHz, CDCl₃): δ = 7.27 (4H). ¹⁹F NMR (282.65 MHz, CDCl₃): δ = -121.5 (1F, dd, cis-CF=CF₂, F_a), -127.4 (1F, dd, trans-CF=CF₂, F_b), -135.2 (1F, dd, CF=CF₂, F_c) (J_{ab} = 72.2, J_{ac} = 43.6, J_{bc} = 82.6). FTIR (KBr): 1833 cm⁻¹ (m, CF=CF₂).

Polymerization of PFCB Monomers. PFCB monomers, distilled and degassed, were placed in a glass tube, which was sealed under a high-vacuum condition. The monomers in the sealed glass tube were bulk polymerized under various conditions, as shown in Table 1. 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. All the polymerization was carried out at 180 °C for 18 h unless otherwise mentioned. The PFCB ring structure in the polymers was typically characterized by multiple peaks of ¹⁹F NMR in the range of -127 to -133 ppm and by FT-IR. When the monomers were polymerized, the CF= CF₂ 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 and optical properties are summarized in Table 2.

Near-IR Spectrum Measurement. Quantitative analysis of fundamental C–H stretching vibrations in the region of $2600-3400 \text{ cm}^{-1}$ was carried out using a KBr liquid cell with 0.5 mm spacer. Overtone bands and combination bands of C–H vibrations were measured using a quartz cell with a path length of 0.2 cm. IR and near-IR spectra of benzene and 1,4-difluorobenzene (2FB) were also measured as reference spectra for the quantitative comparison.

Refractive Index and Birefringence Measurement. Prepared PFCB polymers were dissolved in cyclohexanone at a concentration of 40 wt %. The solution was filtered with a 0.2 μ m Teflon membrane syringe filter. The filtered solution was spin-coated on the silicon wafer substrate at a spin rate of 1000 rpm for 2 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 6–8 μ m. The refractive indices, n_{TE} and n_{TM} of the polymer films, were measured with a Sairon SPA-3000 prism coupler at 1550 nm.

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 a high-vacuum condition. The monomers in the sealed glass tube were polymerized under the conditions summarized in Table 1. 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 a 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. After fiber cut, optical attenuation of the fiber was

Scheme 1. Preparation of Trifluorovinyl Aryl Ether Monomers by Fluoroalkylation and Dehalogenation Reaction







TFVON-co-TFVOB

 Table 1. Molecular Weights and Thermal and Optical Properties of the PTFVON Depending on Various Polymerization

 Condition

PTFVON	temp (°C)	time (h)	$M_{ m n}{}^a$	$M_{ m w}{}^a$	PD	$T_{g}{}^{b}(^{\circ}C)$	$T_{\mathbf{d}^{c}}$ (°C)	optical loss ^d (dB/cm)
PTFVON-1	160	7	2 450	2 657	1.10	98	233	0.576
PTFVON-2	160	12	4 584	6 134	1.34	100	375	0.417
PTFVON-3	180	12	10 878	24 543	2.25	136	388	0.264
PTFVON-4	180	18	21 000	47 300	2.25	138	394	0.240
PTFVON-5	200	24	45 718	121 727	2.66	152	407	0.336

^{*a*} In THF vs polystyrene. ^{*b*} 10 °C/min in N_2 . ^{*c*} Temperature of 5.0% weight loss by TGA at the rate of 10 °C/min in N_2 . ^{*d*} Measured at 1550 nm.

measured again. Optical loss of the fiber was determined by difference of optical attenuation.

Results and Discussion

Monomer Synthesis and Cyclopolymerization. PFCB monomers, TFVON and TFVOB, were synthesized in high purity in two steps: fluoroalkylation with 1,2-dibromotetrafluoroethane and dehalogenation via zinc, as shown in Scheme 1. 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. DMSO and DMF were used as solvents, and their purity was found to be important for achieving a high yield of fluoroalkylated products. The dehalogenation reaction followed a procedure previously reported by Babb and Smith.^{21,24} Monomers were purified by silica gel column chromatography and then vacuum-distilled to remove moisture and impurities. The polymers were obtained by thermal bulk polymerization via $2\pi + 2\pi$ cyclodimerization, as shown in Scheme 2. Polymerization conditions such as temperature and reaction time were very important determinants of thermal properties as well as the optical properties of the synthesized PFCB polymers. These aspects are discussed in a later section of this report.

Table 1 shows the reaction conditions used for the polymerization of poly[1,5-bis(trifluorovinyloxy)naphthalene] (PTFVON). Trifluorovinyl aryl ethers readily dimerize through $2\pi + 2\pi$ cyclodimerization at elevated temperatures, leading to stable perfluorocyclobutane rings.³³ The temperature required for the dimerization depends on the electronic structure of the aryl groups, typically in the range 150–250 °C.^{24,25,34,35} The DSC thermogram of TFVON showed a melting endotherm at 91 °C and a thermal polymerization exotherm at T_{onset} = 153 °C, as shown in Figure 1. Therefore, the thermal bulk polymerization of TFVON was carried out at a



Figure 1. DSC thermograms of TFVON and PTFVON.

temperature above 160 °C. The synthesized polymers, PTFVON-1 and PTFVON-2, had low M_n below 5000 and a relatively low $T_{\rm g}$. When the polymerization temperature was raised to 180 °C, higher molecular weight polymers were obtained (PTFVON-3, -4). The M_n of 20 000 was measured in the case of PTFVON-4 when the polymerization time was increased. The $T_{\rm g}$ and $T_{\rm d}$ of the polymers increased as the polymerization time and temperature were increased, and the T_{g} and T_{d} of PTFVON-4 were measured at 138 and 394 °C, respectively. PTFVON-5 showed better thermal and mechanical properties than the others, but severe vellowing was observed. Most organic polymers are subject to yellowing upon thermal aging due to thermal oxidation leading to the formation of conjugated molecular structures. Yellowing can be minimized when the polymerization was performed under inert atmosphere or under vacuum. Therefore, we polymerized all the monomers in sealed tubes under vacuum. Nevertheless, this yellowing phenomenon was difficult to avoid in our experiments especially when the polymerization was carried out at a higher temperature or when a longer polymerization time was used.

As discussed above, the naphthalene-based PFCB polymer, PTFVON, was successfully prepared and showed high T_g and T_d , as expected. However, the number of remaining C–H bonds was still quite large. Therefore, we also synthesized a phenylene-based PFCB polymer, PTFVOB, which has a lower fraction of C–H bonds. Because PTFVON, prepared at 180 °C for 18 h, had a high molecular weight and low yellowing, 1,4-bis(trifluorovinyloxy)benzene (TFVOB) was polymerized under the same conditions. A DSC thermogram of TFVOB also showed a similar polymerization exotherm ($T_{\text{onset}} = 160$ °C) to that of TFVON. The PTFVOB had a relatively low T_g of 41 °C due to the smaller aromatic group compared to the naphthalene of PTFVON.

The molecular weights and thermal and optical properties of the polymers are summarized in Table 2. Copolymerization generally induces a more amorphous morphology via effectively introducing the irregularity; therefore, TFVON and TFVOB were also copolymerized in 1:1 ratio (wt %) under the same conditions. The



Figure 2. Refractive indices and birefringence of PFCB polymer films at 1550 nm.

copolymer showed a $T_{\rm g}$ of 91 °C, which is an intermediate value between the $T_{\rm g}$ s of PTFVON and PTFVOB, indicating the random copolymerization of two monomers. The molecular weights ($M_{\rm n}$) of the polymers were typically 20 000. The prepared PFCB polymers showed good solubility in common organic solvents such as THF, chloroform, and toluene. Excellent optical quality films could be prepared by spin-coating.

Optical properties such as refractive index and birefringence of the polymer films were measured, as shown in Figure 2. Refractive indices of the polymers were in the range 1.44–1.50, and PTFVOB had a low refractive index of 1.4446 due to its high fluorine content. PT-FVON showed a higher refractive index due to the larger aromatic content, and the copolymer exhibited an average value between the two homopolymers. The birefringence of the spin-coated films of the PFCB polymers was investigated and found to be exceptionally low. A Δn of less than 0.001 was measured in all the polymers. The lowest birefringence of 0.0005 was measured for PTFVON films. This may be due to the amorphous polymer structure resulting from the random arrangement of cis- and trans-1,2-disubstituted PFCB rings.³³ In addition, these birefringence values were much lower than previously reported data for biphenyl-based PFCB and triphenylethane-based PFCB polymers.^{19,20,35} Birefringence is, in general, caused by stress during the film preparation. In particular, the high rate of spinning during the spin-coating process causes the polymer chains to extend in a direction parallel to the film plane. Therefore, in such cases, the refractive index in the TE mode is larger than that of the TM mode. This higher refractive index in the TE mode can be canceled by the incorporation of a structural unit that has high polarizability in the direction perpendicular to the polymer backbones. Because of this, the 1,5 linkage of naphthalene in the PTFVON

Table 2. Molecular Weights and Thermal and Optical Properties of the PFCB Polymers and Copolymer

PFCB	$M_{ m n}{}^a$	$M_{ m w}{}^a$	T_{g}^{b} (°C)	$T_{\mathbf{d}}{}^{c}$ (°C)	hydrogen content ^d	n_{TE}^{e}	n_{TM}^{e}	Δn^{e}
PTFVON	21 000	47 300	138	394	19.4	1.4999	1.4994	0.0005
PTFVOB	16 200	22 100	41	397	16.6	1.4455	1.4446	0.0009
TFVON-co-TFVOB	18 000	39 500	91	340	18	1.4795	1.4788	0.0007

^{*a*} In THF vs polystyrene. ^{*b*} By DSC at the rate of 10 °C/min in N₂. ^{*c*} Temperature of 5.0% weight loss by TGA at the rate of 10 °C/min in N₂. ^{*d*} % of the number of C–H bond per the total number of bonds in the repeating unit. ^{*e*} Measurement at 1550 nm.



Figure 3. FT-IR spectra of TFVOB and PTFVOB.

polymer backbones is believed to show a very low birefringence. This is consistent with the relatively higher birefringence ($\Delta n = 0.005$) of biphenyl-based PFCB polymers,³⁵ where the polarizability of biphenyl groups would be the largest in the direction parallel to the extended polymer backbones.

To confirm this hypothesis, we measured s- and p-polarized UV-vis spectroscopy spectra as a function of tilt angle of incident beam to investigate the alignments of naphthalene moiety in the spin-coated film. However, unfortunately we could not confirm the naphthalene alignment due to their very low degree of orientation (birefringence of 10^{-4} in our case). Some other materials tested having the birefringence of 10^{-3} in our laboratory could show detectable differences in the polarized spectra and orientation tendency; however, the materials with 10^{-4} birefringence did not reveal clear difference between TE and TM modes. For optical waveguide devices, low birefringence is a key requirement,¹ and from that sense, PFCB polymers represent good candidates for polymer waveguide materials with low birefringence.

IR and Near-IR Spectrum Analysis. Figure 3 shows the FTIR spectra of TFVOB and PTFVOB, which reveal two types of important information: one is the confirmation of the polymerization and the other is the estimation of the intrinsic optical loss by C-H vibrational absorption. When the monomers were polymerized, the $CF=CF_2$ stretching vibration peak at 1833 cm⁻¹ disappeared, and a new PFCB ring peaks appeared at 965 cm⁻¹. Thus, the polymerization could be confirmed by the difference in the intensity of the two peaks.²² In addition, the C-H stretching vibration peaks of TFVOB and PTFVOB in 3000-3400 cm⁻¹ contained information concerning optical loss at visible and near-IR region. If the intensity of the C-H fundamental stretching vibration is strong, the overtone band strength will be increased, and as a result, a large optical loss in the visible and near-IR region would be expected.

As shown in Figure 3, the C-H fundamental stretching vibrations for both TFVOB and PTFVOB were observed to be very low compared to the other peaks, despite the presence of the four C-H bonds on each aromatic ring. This can be attributed to the strong electronic effects of fluorine atoms substituted near the aromatic ring. The naphthalene-based TFVON and PTFVON also exhibited low C-H vibrational intensity,



Figure 4. FT-IR spectra of the PFCB monomer, TFVOB, and reference compounds in the region of C–H fundamental stretching vibration.

even though the effect was more evident in the case of the phenylene-based TFVOB and PTFVOB. PFCB polymers prepared in this study contain a high density of fluorine substituents on the aromatic conjugated systems through ether linkage; therefore, a strong inductive electron-withdrawing effect would be applied to the aromatic rings, leading to an decrease of bond length and an increase of the vibrational frequencies of C-H bonds.^{36,37} Electron-withdrawing linkages other than fluorine, such as sulfone, also exhibit similar effects as recently reported.¹¹ Even though those relationships between electronic effects and the vibrational frequencies are quite well-known, to our knowledge, the intensity of the C-H bond in these cases is not clearly understood to date. As shown in Figure 3, the reduction in C-H vibrational intensity was quite remarkable in these compounds; therefore, low vibrational absorption loss at near-IR region may be expected.

To measure the intensity of vibrational absorption of C-H bonds in these monomers and polymers, fundamental C-H stretching vibrations of the PFCB monomers in the region of 3000-3400 cm⁻¹ were measured using a KBr liquid cell with a 0.5 mm spacer. The IR spectra of benzene and 1,4-difluorobenzene (2FB) were also measured as reference spectra. The monomer TFVON was not measured because it was a solid at room temperature. Figure 4 shows the FTIR spectra for the TFVOB and reference compounds with the same path length in the region of 2600–3400 cm⁻¹. Compared to benzene, it is clear that the C-H intensity of TFVOB was dramatically reduced. However, an exact quantification was difficult because the peaks were overlapped with many other peaks, largely consisting of higher harmonics of lower frequency vibrations.

The overtone and combination bands of C-H vibrations of the TFVOB monomer and reference compounds were also measured using a quartz cell with a path length of 0.2 cm in the near-IR region, as shown in Figure 5. The first overtone bands (2v) of the aromatic C–H fundamental vibrations (1v), the first combination bands ($2v + \delta$) of the C–H stretching and bending, and the second overtone bands (3v) appeared in the region of 2000-1550, 1300-1500, and 1100-1200 nm, respectively. The near-IR spectrum would be still difficult to analyze due to a number of overtone and combination bands of various stretching vibrations, for example C-O bonds, C–C bonds, and C=C bonds.³⁸ The absorption peaks in the region of the first overtones and combination bands were very complicated, but the complexity of the second overtone bands was reduced compared to



Figure 5. Comparison of C–H vibrational intensity of PFCB monomers with 1,4-difluorobenzene (2FB) and benzene in the near-infrared region.

the lower overtones and combination bands. Because of this, the effects of fluorination on the C-H vibrational overtones were more clearly observed in the second overtone band region. The hydrogen content of TFVOB, 2FB, and benzene, defined as percent of the number of C-H bond per the total number of bonds in the repeating unit,¹³ was 16.6, 33.3, and 50%, respectively. When the hydrogen content was compared with the intensity of peak absorbance at the second C-H overtone bands, we found that the intensity of C-H overtone absorption of fluorinated materials was largely reduced. The hydrogen content of TFVOB was reduced to onethird of benzene; however, the intensity at peak absorbance was reduced to about one-fourth of benzene. This additional reduction of vibrational C-H overtone intensity is believed to result from the fluorine substitution because even for the 2FB, the similar intensity reduction was observed. This result may indicate that the partially fluorinated polymers may show much lower optical loss than expected if properly substituted. Detailed studies on this phenomenon including quantum mechanical calculation are under way.

In addition, the peaks for the fluorinated materials were shifted about 15 nm to shorter wavelength compared to those of benzene. This is likely due to the δ -electron withdrawing effect of fluorine, which leads to a decrease in C-H bond length and an increase in the C–H frequencies.^{36,37} Thus, the proper substitution of an aryl group could be used to tailor the C-H absorption so as to be either shifted or retained. This frequency shift is important from two aspects. First, it can significantly affect optical loss at a fixed optical source wavelength.¹⁷ Second, the absorption frequency shift also determines the position of the low loss optical windows. Especially for POF applications, the optical window position should be matched with the optical source for the longer transmission. In the spectra shown in Figure 5, the wavelengths of the optical telecom source at 1300, 1310, and 1550 nm seem to be quite far from the vibrational frequencies, and absorption at those wavelengths looks negligible.^{19,39} However, because the measurement was performed with a relatively short path length, it was difficult to estimate the optical loss quantitatively in these wavelengths from the results, reported here.

Optical Loss of PFCB Polymers. Only limited information is available in the literature regarding the optical loss of PFCB polymers. Petermann et al. studied waveguides using a triphenylethane-based PFCB poly-



Figure 6. Optical loss of PTFVON at 1550 nm polymerized under different conditions.

mer and reported a value of 0.25 dB/cm at 1515-1565 nm.¹⁹ Smith et al. also reported that the attenuation loss was consistent with the reported value or could be lower than previously reported values.^{20,39} However, optical loss spectra or optical windows of PFCB polymers in the near-IR region have not yet been reported. As discussed earlier, we investigated C-H overtone bands of PFCB monomers, which showed negligible absorption in the optical sources. However, the path length of 0.2 cm in the quartz cell was too short to determine the exact optical loss and optical windows in the near-IR region. Therfore, we fabricated PFCB polymers as plastic optical fibers having a sufficient path length and carried out measurements of optical loss and windows in the region of 700–1600 nm.

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, impurities, and an extrinsic loss factor due to structure imperfections. In addition, PFCB polymers showed a slight yellowing, when polymerized at temperatures above 160 °C, and the yellowing was more severe for long polymerization times and temperatures. Because yellowing affects optical loss in the short wavelength,^{1,10} we examined this aspect as a function of polymerization conditions. A randomly distributed copolymerization would also lead to a more amorphous structure than a homopolymer. Because of this, a PFCB amorphous copolymer, TFVON-*co*-TFVOB, was prepared, and the optical loss was measured.

Figure 6 shows optical loss changes as a function of various polymerization conditions as summarized in Table 1. When polymerized at 160 °C for 7 h, PTFVON-1, although transparent, was brittle and generated a number of voids during the drawing process, probably due to unpolymerized monomers. The optical loss of PTFVON-1 was 0.6 dB/cm at 1550 nm. As the polymerization time increased, the molecular weights and the temperature at which a 5% weight loss of PTFVON-2 occurred were about doubled, and the optical loss of PTFVON-2 was reduced by nearly 50%. In the cases of PTFVON-3 and PTFVON-4, the optical loss was steadily reduced, and PTFVON-4 had a low loss of 0.227 dB/cm, which was in the same range as those reported for PFCB polymers.^{19,20,39} The reduction in the optical loss for the PTFVON-1-4 can be attributed to an increase in the molecular weight and corresponding improvement of thermal and mechanical stability during fiber drawing. However, when polymerized at 200 °C for 24 h the optical loss abruptly increased. As discussed earlier, it is likely that the increase in optical loss mainly resulted

Table 3. Optical Loss of the PFCB Polymers at Low Loss Window and Optical Source

	optical loss (dB/cm)								
	optical loss window (nm)					optical source (nm)			
polymer	820	910	1025	1260	1530	1300	1310	1550	
PTFVON-4 TFVON- <i>co</i> -TFVOB	0.092 0.082	0.083 0.080	0.097 0.087	0.120 0.092	0.225 0.200	0.190 0.156	0.218 0.181	0.227 0.200	



Figure 7. Optical loss spectrum of PTFVON (–) and TFVON*co*-TFVOB (- - -) in the region of 700–1600 nm.

from severe yellowing by thermal aging during the polymerization or by thermal degradations during fiber drawing at a high temperature due to the higher T_g of PTFVON-5.^{1,10,40}

Figure 7 shows optical attenuation spectra of the PFCB polymers. The second overtone bands 3v and the third overtone bands 4v were in the regions 1050-1250and 815–910 nm, and the first combination bands 2v $+ \delta$ and the weak second combination bands $3v + \delta$ were in the regions 1250-1530 and 910-1050 nm, respectively. Both homo- and copolymer exhibited similar attenuation spectra. As expected, the attenuation became smaller as the wavelength became smaller because intensities of the higher vibrational overtones become weaker. However, below 800 nm, the attenuation increased again with decreasing wavelength. The optical loss factors that were dominant in the short wavelength region are known to be Rayleigh scattering and electronic transitions. In our case, yellowing would be another important loss factor in the short wavelength regions.

Optical windows were observed at 820, 910, 1025, 1260, and 1530 nm. Table 3 shows the loss values of the PFCB polymers at the optical windows and optical sources. The attenuation loss of PTFVON-4 was 0.083 dB/cm at 910 nm, the lowest optical window, 0.190 dB/ cm at 1300 nm, and 0.227 dB/cm at 1550 nm. The loss of the copolymer, TFVON-co-TFVOB, would be expected to show a lower loss due to increased fluorine contents and more amorphous morphology. The loss of TFVONco-TFVOB was about 0.080 dB/cm at 910 nm of the lowest optical window, 0.156 dB/cm at 1300 nm, and 0.20 dB/cm at 1550 nm. The optical loss for the copolymer was about 0.003-0.01 dB/cm lower than PTFVON-4. The major factors contributing to optical loss are thought to be intrinsic loss due to higher harmonics of aromatic C-H vibrations and absorption by yellowing at a short wavelength region. However, several extrinsic loss factors should also contribute significantly to the total attenuation of the fiber because the optical fiber formation process we employed was not optimized. These factors could include monomer purity, microvoids in fibers, and especially the lack of existing cladding. At the present time it is difficult to evaluate the extent to which the extrinsic factors contribute to the loss, but the attenuation loss could be greatly lowered by the optimization of the polymerization and processing.

Conclusion

We successfully synthesized new PFCB monomers and corresponding homo- and copolymers from them through $2\pi + 2\pi$ cyclopolymerization. Thermally stable polymers with relatively high $T_{\rm g}$ could be obtained. For naphthalene-based polymers PTFVON, $T_{\rm g}$ and $T_{\rm d}$ of PTFVON were measured at about 140 and 400 °C, respectively. Phenylene-based low- $T_{\rm g}$ PFCB polymer PTFVOB and a random copolymer of the two monomer were also successfully obtained. The birefringence of the spin-coated films of the PFCB polymers was found to be lower than 0.001.

The optical absorption properties of the PFCB polymers were investigated via IR and near-IR spectra and as well as their optical loss as plastic optical fibers. The findings show that the C–H absorption intensity of PFCB monomers was dramatically reduced in the IR and near-IR region. This could lead to a significant reduction in optical attenuation loss of the final polymers. When the polymerization was carried out, the optical loss varied from 0.6 to 0.2 dB/cm depending on the polymerization conditions. In addition, the optical loss of the copolymer was about 0.003-0.01 dB/cm lower than that of the homopolymer. As a result, the optical loss values were strongly dependent on the polymerization conditions.

We first prepared plastic optical fibers of the PFCB polymers, and optical windows were observed at 820, 910, 1025, 1260, and 1530 nm. The attenuation loss of PTFVON was typically 0.083 dB/cm at 910 nm, the lowest optical window, 0.19 dB/cm at 1300 nm, and 0.227 dB/cm at 1550 nm. However, these loss values could be greatly improved by optimizing the polymerization and processing. Along with low birefringence, good processability, thermal properties, and low optical loss, PFCB polymers represent promising candidates for use in polymer photonic devices.

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