# Synthesis and Properties of Partially Fluorinated Amorphous Ring Containing Polymers: Poly[bis(2,2-difluorovinyl)formal], Poly[bis(2,2-difluorovinyl)difluoroformal], and Poly[bis(1-deuterio-2,2-difluorovinyl)difluoroformal]

**Yu Yang,[†] František Mikeš,[†] Yasuhiro Koike,[‡] and Yoshiyuki Okamoto*,[†]**

*H. F. Mark Polymer Research Institute, Polytechnic University, 6 MetroTech Center, Brooklyn, New York 11201, and Faculty of Science and Technology, Keio University, Yokohama 223-8522, and ERATO, Koike Photonics Polymer Project, K2 Town Campus Kawasaki 212-0054, Japan*

*Received March 18, 2004; Revised Manuscript Received July 26, 2004*

ABSTRACT: Three novel partially fluorinated monomers, bis(2,2-difluorovinyl)formal (I), bis(2,2-difluorovinyl)difluoroformal (II), and bis(1-deuterio-2,2-difluorovinyl)difluoroformal (III), were prepared. These monomers were polymerized in bulk via free radical mechanism. Monomer I produced a cross-linked polymer, but monomers II and III yielded amorphous polymers (II-P and III-P) having five- and six-membered rings along the backbone. Polymers II-P and III-P were soluble not only in fluorinated solvents but also in nonfluorinated solvents such as THF, 1, 4-dioxane, DMF, and DMSO. They have good thermal stability (onset of decomposition >400 °C), high glass transition temperatures (105 °C), and low dielectric constant (1.98−1.82 at frequency ranging from 0.1 to $3 \times 10^6$ Hz). Furthermore, these polymers are completely amorphous and possess outstanding optical clarity extending from visible to near-IR regions. The refractive indices of both polymers were measured at various wavelengths to evaluate material dispersion. The material dispersions of II-P and III-P were similar and had low values, which are comparable to perfluorinated polymers and much lower than perdeuterioPMMA. The unique optical properties of these polymers make them attractive for use as optical materials.

## Introduction

Since the demonstration of the first plastic optical fibers (POF) in the 1960s, POF has been increasingly applied to local area network (LAN) because of its high elastic moduli, easy mechanical and optical coupling, low installation cost, etc.[1,2] As a result of these advantages, various POF materials have been developed such as poly(methyl methacrylate) (PMMA), polycarbonate (PC), and polystyrene (PS). PMMA has excellent transparency, permits mass production, and is of low cost. However, the carbon−hydrogen bonds in PMMA cause strong optical absorption in visible and near-infrared wavelengths, even at the best transparent windows around 570 and 520 nm.[3] When the hydrogen atoms in PMMA are replaced with heavier atoms such as deuterium[4,5] and fluorine,[6] the optical absorption is decreased. The attenuation of an all-deuterium-substituted PMMA-$d_8$ based graded index GI-POF at 650 nm wavelength is about 60 db/km, which is approximately half of the attenuation of a GI-POF based on the hydrogen-substituted PMMA.[7] The partially fluorine-substituted acrylate, 1,1,1,2,2,2-hexafluoroisopropyl 2-fluoroacrylate (HFIP 2FA), in which only three carbon−hydrogen bonds exist, also exhibits decreased optical absorption at around 780 nm.[8] The attenuation of its GI-POF at 780 nm is 158 db/km. This is much lower than that of the PMMA (785 db/km at 780 nm). It was also found that the introduction of fluorine atoms into polymers not only effectively decreased the attenuation but also greatly lowered material dispersion and thus greatly increased the bandwidth.[8]

POF require polymers to have high enough glass transition temperature for high-temperature working conditions. It is well-known that bulky rings along the polymer backbone would greatly increase the glass transition temperature of the polymer. Cyclopolymerization of diene monomers is one of the most effective methods for the preparation of polymers having cyclic structures in their main chain. The nonconjugated divinyl monomers are known to be cyclopolymerizable monomers. Free radical polymerization of divinyl formal, acetaldehyde divinyl acetal, and acetone divinyl ketal have been reported.[12] The polymerizations of these monomers were carried out under various conditions. When the conversions were kept below 10%, the isolated polymers contained five-membered ring structures while six-membered rings were not detected. As the conversion increased, pendant vinyl groups and gel formation were observed in the polymers.[12]

If the hydrogen atoms in the divinyl formal are substituted with fluorine and/or deuterium, the reactivity of the monomers and properties of the polymers produced may change. Thus, we have synthesized three monomers I, II, and III (Figure 1), which contain different amount of hydrogen, deuterium, and fluorine atoms. The polymerizations of monomers and the properties of the polymers prepared were investigated as well. Monomers were prepared according to Scheme 1.

## Experimental Section

**Materials**. Methyl chlorodifluoroacetate (99%) was obtained from SynQuest Chemical Co. Fluorinert FC-75 (a fluorinated solvent) was obtained from 3M Co. All other chemicals were purchased from Aldrich Chemical Co. All reagents were used without further purification. Perfluorodibenzoyl peroxide (F-

[†] Polytechnic University.
[‡] Keio University.
* Corresponding author. E-mail: yokamoto@poly.edu.

10.1021/ma049462d CCC: $27.50 © 2004 American Chemical Society
Published on Web 09/21/2004

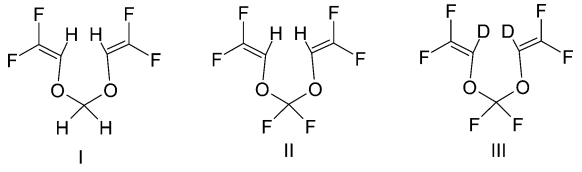
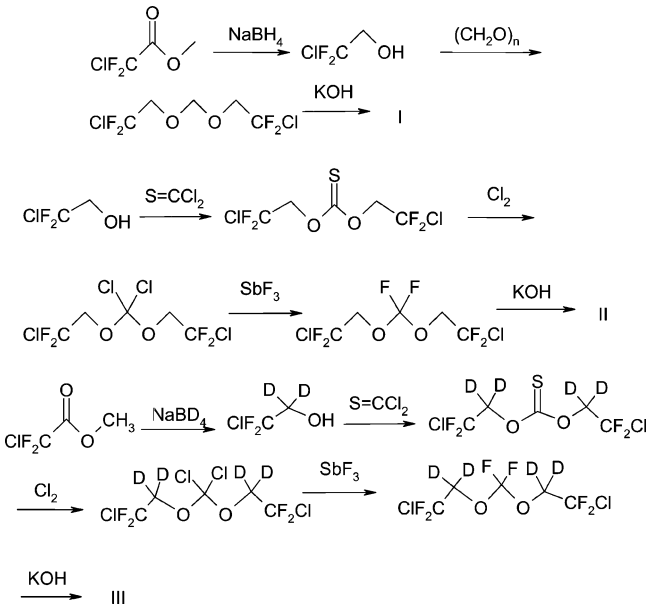


**Figure 1.** Chemical structures of bis(2,2-difluorovinyl)formal (I), bis(2,2-difluorovinyl)difluoroformal (II), and bis(1-deuterio-2,2-difluorovinyl)difluoroformal (III).

**Scheme 1. Synthesis Routes for Monomers I, II, and III**



BPO) was prepared according to published procedure.[14] The crude initiator was recrystallized from petroleum ether (bp 40−60 °C), and purified initiator has a melting point of 76−78 °C; its half-life at 68 °C is 10 h.[15]

**Instrumentation**. $^{19}F$ and $^{1}H$ NMR spectra were obtained on a Bruker AC-300 spectrometer in $CDCl_3$ containing 1% TMS as an internal reference. The IR spectra were measured on a Perkin-Elmer 1600 series FTIR. GC MS measurements were conducted using a 5970 series by Hewlett-Packard Co. The refractive indices of the polymer were measured using a Metricon model 2010 prism coupler thin film thickness/refractive index measurement system made by Metricon Corp. Thermal properties were determined using a TA Instruments Inc. DSC 2920 differential scanning calorimeter and a Hi-Res Modulated TGA 2950 thermogravimetric analyzer. SEC analysis was carried out using Waters Eupower Software with a Waters 510 pump and a Waters 2414 refractive index detector under the following conditions: Polymer Laboratory PLgel 10000A and PLgel 5000A as columns and THF eluent at a flow rate of 1.0 mL/min. The calibration curves for SEC analysis were obtained using polystyrene standards.

**Preparation of Bis(2,2-difluorovinyl)formal (I) and Its Polymer (Polymer I-P). Synthesis of 2-Chloro-2,2-difluoroethanol.** A solution of 500 g (3.461 mol) chlorodifluoroacetate in 200 mL of diethyl ether was added dropwise to a refluxed and stirred solution of 137 g (3.621 mol) of sodium borohydride, 800 mL of diethyl ether, and 17 mL of methanol. After refluxing for 3 h the reaction mixture was cooled. Then 300 mL of 2 N aqueous solution of hydrochloric acid was added, and the water layer was twice extracted with 400 mL of diethyl ether. Combined ether solutions were dried over anhydrous magnesium sulfate. Rectification on a packed column yields 314 g (2.695 mol) of 1-chloro-2, 2-difluoroethanol with boiling point of 95−96 °C/760 Torr. $^{1}H$ NMR: $\delta$ 3.80 (s, −OH, 1H), 3.99 (t, $^{3}J_{H-F}$ = 10.9 Hz, $-CH_2-$, 2H). $^{19}F$ NMR: $\delta$ −65.1 (t, $^{3}J_{H-F}$ = 10.9 Hz, $-CF_2Cl$, 2F). $^{13}C$ NMR: $\delta$ 127.8 (t, $^{1}J_{C-F}$ = 293.6 Hz, $-CF_2Cl$), 66.7 (t, $^{3}J_{C-F}$ = 29.3 Hz, $-CH_2-$). Anal. Calcd for $C_2H_3F_2ClO$: C, 20.62; H, 2.57; Cl, 30.46. Found: C, 20.13; H, 2.44; Cl, 30.20%.

**Synthesis of Bis(2-chloro-2,2-fluoroethyl)formal.** To a flask containing a mixture of 22.6 g (0.710 mol) of $(CH_2O)_n$ and 50 mL of 98% sulfuric acid was added 116.5 g (1.000 mol) of 2-chloro-2,2-difluoroethanol. After addition, stirring continued for 3 h at room temperature. The reaction solution was poured into 300 mL of ice water. The organic layer was separated and dried with anhydrous magnesium sulfate. After filtering and rectification on a packed column, 72.5 g (0.340 mol) of pure product was obtained, and the yield was 68% (bp 160 °C/760 Torr.). $^{1}H$ NMR: $\delta$ 4.84 (s, $OCH_2O$, 2H), 4.04 (t, $^{3}J_{H-F}$ = 10.9 Hz, $CF_2ClCH_2-$, 4H). $^{19}F$ NMR: $\delta$ −62.6 (t, $^{3}J_{H-F}$ = 10.9 Hz, $-CF_2Cl$, 4F). $^{13}C$ NMR: $\delta$ 126.5 (t, $^{1}J_{C-F}$ = 293.0 Hz, $-CF_2Cl$), 70.7 (t, $^{3}J_{C-F}$ = 28.8 Hz, $-CH_2-$), 95.7 (s, $-O-CH_2-$), Anal. Calcd for $C_5H_6F_4Cl_2O_2$: C, 24.49; H, 2.45; Cl, 28.97. Found: C, 24.29; H, 2.32; Cl, 28.40%.

**Synthesis of Bis(2,2-difluorovinyl)formal.** To 65.9 g (1.0 mol) of molten 85% KOH at 190 °C was slowly added 14 g (57.1 mmol) of $CF_2ClCH_2OCH_2OCH_2CF_2Cl$ for 30 min. The reaction product was condensed in a dry ice trap. The condensed 8.5 g of liquid was distilled, and 6.2 g (36.0 mmol) of pure monomer I was isolated with a yield of 63%.

$CF_2{=}CHOCH_2OCH{=}CF_2$: bp 96 °C/760 Torr. $^{1}H$ NMR: $\delta$ 4.89 (s, $OCH_2O$, 2H), 5.82−5.88 (dd, $^{3}J_{\text{trans H-F}}$ = 12.0, $^{3}J_{\text{cis H-F}}$ = 3.0, $CF_2{=}CH$, 2H). $^{19}F$ NMR: $\delta$ −98.9 to −99.2 (dd, $^{3}J_{\text{trans H-F}}$ = 12.0, $^{2}J_{F-F}$ = 71.0, 2F), −118.4 to −118.7 (d, $^{3}J_{\text{cis H-F}}$ = 3.0, $^{2}J_{F-F}$ = 71.0, 2F). $^{13}C$ NMR: $\delta$ 105.7 (dd, $^{2}J_{\text{cisC-F}}$ = 16.0 Hz, $^{2}J_{\text{transC-F}}$ = 46.7 Hz, $-CH-$), 96.4 (s, $-OCH_2O-$), 156.2 (dd, $^{1}J_{C-F}$ = 277.0 Hz, $^{1}J_{C-F}$ = 288.6 Hz, $=CF_2$). IR: 1173 $cm^{-1}$ (C=C). MS, *m/e* 172 (M+).

1.2 g (5.7 mmol) of higher boiling fraction was $CF_2{=}CHOCH_2$-$OCH_2CF_2Cl$ (yield 10%): bp 129 °C/760 Torr. $^{1}H$ NMR: $\delta$ 4.89 (s, $-OCH_2O-$, 2H), 4.02−4.09 (t, $^{3}J_{H-F}$ = 11.0 Hz, $CF_2ClCH_2$, 2H), 5.80−5.87 (dd, $^{3}J_{\text{trans H-F}}$ = 15.0, $^{3}J_{\text{cis H-F}}$ = 3.0, $CF_2{=}CH-$, 1H). $^{19}F$ NMR: $\delta$ −99.1 to −99.4 (dd, $^{3}J_{\text{trans H-F}}$ = 15.0, $^{2}J_{F-F}$ = 72.0, 1F), −118.2 to −118.5 (d, $^{3}J_{\text{cis H-F}}$ = 3.0, $^{2}J_{F-F}$ = 72.0, 1F), −62.7 (t, $^{3}J_{H-F}$ = 11.0, $-CF_2Cl$, 2F). $^{13}C$ NMR: $\delta$ 105.5 (dd, $^{2}J_{\text{cisC-F}}$ = 15.5 Hz, $^{2}J_{\text{transC-F}}$ = 46.4 Hz, $=CHO-$), 96.1 (s, $-OCH_2O-$), 156.0 (dd, $^{1}J_{C-F}$ = 277.0 Hz, $^{1}J_{C-F}$ = 288.0 Hz, $=CF_2$), 126.5 (t, $^{1}J_{C-F}$ = 277.0 Hz, $-CF_2Cl$), 70.8 (t, $^{3}J_{C-F}$ = 29.0 Hz, $-OCH_2-$). IR: 1173 $cm^{-1}$ (C=C). MS, *m/e* 208, 210 (M+).

**Polymerization of Bis(2,2-difluorovinyl)formal.** In an ampule was added 0.8 g of monomer and 0.01 g of F-BPO initiator. After the mixture was degassed, the ampule was sealed. The polymerization was carried out at 50 °C for 1 day. The precipitated polymer was washed with chloroform. The solid polymer was dried in a vacuum at 60 °C for 1 day, and 0.7 g of polymer was obtained. The polymer I-P is insoluble in various organic solvents such as THF, DMSO, DMF, 1,4-dioxane, benzene, hexafluorobenzene, 1,1,2-trichloro-1,2,2-trifluoroethane, trifluoroethanol, trifluoroacetic acid, and Fluorinert FC-75.

**Preparation of Bis(2,2-difluorovinyl)difluoroformal (II) and Its Polymer (II-P). Bis(2-chloro-2,2-difluoroethyl)thionocarbonate.** To a solution of 81.6 g (700.0 mmol) of 2-chloro-2,2-difluoroethanol in 560 mL of water at 10 °C was added 70 mL of 10 N sodium hydroxide aqueous solutions. Then with vigorous stirring, a solution of 28 mL of thiophosgene (350.0 mmol) in 42 mL of $CH_2Cl_2$ was added dropwise over 20 min at 15 °C. Stirring was continued at room temperature. The $CH_2Cl_2$ phase was separated and dried with $MgSO_4$. After solvent was removed, the residue was distilled at 64−66 °C/11 Torr to give 75.5 g (262.5 mmol) of product (yield 75%). $^{1}H$ NMR: $\delta$ 4.92 (t, $^{3}J_{H-F}$ = 10.3 Hz, $CH_2$, 2H). $^{19}F$ NMR: $\delta$ −62.0 (t, $^{3}J_{H-F}$ = 10.3 Hz, $-CF_2Cl$, 2F). $^{13}C$ NMR: $\delta$ 73.4 (t, $^{2}J_{C-F}$ = 91.0 Hz, $-CH_2-$), 192.7 (s, $-OCSO-$), 124.4 (t, $^{1}J_{C-F}$ = 293.9 Hz, $-CF_2Cl$). Anal. Calcd for $C_5H_4F_4$-$Cl_2O_2S$: C, 21.83; H, 1.47; Cl, 25.78. Found: C, 21.50; H, 1.70; Cl, 25.03%.

**Bis(2-chloro-2,2-difluoroethyl)dichloroformal.** 100 g of gaseous chlorine was passed into a stirred solution of 96.3 g (350 mol) of bis(2-chloro-2,2-difluoroethyl)thionocarbonate in 100 mL of $CH_2Cl_2$ for 6 h at room temperature. After filtering

off a small amount of white precipitate, volatiles were removed under reduced pressure. The residual oil was distilled at 62−68 °C/12 Torr and yielded 101.5 g (91%) of the product. $^1$H NMR: $\delta$ 4.45 (t, $^3J_{C-F}$ = 10.0 Hz, $CH_2$, 2H). $^{19}$F NMR: $\delta$ −62.1 (t, $^3J_{H-F}$ = 10.0 Hz, $-CF_2Cl$, 2F). $^{13}$C NMR: $\delta$ 70.6 (t, $^2J_{C-F}$ = 31.0 Hz, $-CH_2-$), 121.9 (s, $-OCCl_2O-$), 124.5 (t, $^1J_{C-F}$ = 292.5 Hz, $-CF_2Cl$). Anal. Calcd for $C_5H_4F_4Cl_4O_2$: C, 19.13; H, 1.28; Cl, 45.18. Found: C, 19.06; H, 1.30; Cl, 44.6%.

**Bis(2-chloro-2,2-difluoroethyl)difluoroformal.** Into a flamed flask under an argon atmosphere charged with 1.79 g (10.0 mmol) of $SbF_3$, 10 mL of $CH_3CN$, and 0.01 g of bromine, 3.16 g (10.0 mmol) of bis(2-chloro-2,2-difluoroethyl)dichloroformal was added dropwise at room temperature under stirring. After half an hour 30 mL of $CH_2Cl_2$ was added, and the reaction solution mixture was poured into water. The organic layer was washed with 40 mL of water, 40 mL of 1 N HCl aqueous solution, and 10 mL of brine and then dried using anhydrous $MgSO_4$. Redistillation gave 2.22 g (8 mmol) of pure bis(2-chloro-2,2-difluoroethyl)difluoroformal (bp 128−132 °C/ 760 Torr) in 80% yield. $^1$H NMR: $\delta$ 4.13 (t, $^3J_{H-F}$ = 10.3 Hz, 4H). $^{19}$F NMR: $\delta$ −63.3 (tt, $^3J_{H-F}$ = 10.3 Hz, $^5J_{F-F}$ = 2.1 Hz, $-CF_2Cl$, 4F), −64.1 (quintet, $^4J_{H-F}$ = 2.1 Hz, $-OCF_2O-$, 2F). $^{13}$C NMR: $\delta$ 68.1 (tt, $^2J_{C-F}$ = 31.0 Hz, $^3J_{C-F}$ = 3.6 Hz, $-CH_2-$), 121.9 (t, $^1J_{C-F}$ = 254.6 Hz, $-OCF_2O-$), 124.5 (t, $^1J_{C-F}$ = 292.7 Hz, $-CF_2Cl$). Anal. Calcd for $C_5H_4F_6Cl_2O_2$: C, 21.37; H, 1.44; Cl, 25.24. Found: C, 21.25; H, 1.48; Cl, 24.48%.

**Bis(2,2-difluorovinyl)difluoroformal.** A mixture of bis-(2-chloro-2,2-difluoroethyl)difluoroformal (25.0 g, 89.73 mmol), KOH (17.6 g, 270 mmol), and 9 mL of DMSO was refluxed. The product was purified by distillation using a spinning band distillation apparatus to give 14.4 g (69.4 mmol) of bis(2,2-difluorovinyl)difluoroformal (bp 60−62 °C/ 760 Torr) with a yield of 77.3%. $^1$H NMR: $\delta$ 4.10 (ddt, $^3J_{trans H-F}$ = 13.2 Hz, $^3J_{cis\ H-F}$ = 3.8 Hz, $^4J_{H-F}$ = 0.6 Hz, 2H). $^{19}$F NMR: $\delta$ −65.6 (t, $^5J_{F-F}$ = 2.1 Hz, 2F, $-OCF_2O-$), −93.6 (ddt, $^3J_{trans\ H-F}$ = 13.4, $^2J_{F-F}$ = 57.7, $^5J_{F-F}$ = 2.1 Hz, 2F, F at vinyl and trans to H, 1F), −112.3 (dd, $^3J_{cis\ H-F}$ = 4.1, $^2J_{F-F}$ = 57.7, 2F, F at vinyl and cis to H, 1F). $^{13}$C NMR: $\delta$ 155.4 (dd, $^1J_{C-F}$ = 293.0 Hz, $^1J_{C-F}$ = 280.3 Hz, $=CF_2$), 99.0 (ddt, $^2J_{C-F}$ = 60.8 Hz, $^2J_{C-F}$ = 16.0 Hz, $^4J_{C-F}$ = 3.9 Hz, $=CFO-$), 119.6 (tm, $^1J_{C-F}$ = 256.0 Hz, $-OCF_2O-$). IR: 1173 cm$^{-1}$ (C=C). MS, *m/e* 208 (M+)

**Polymerization of Bis(2,2-difluorovinyl)difluoroformal.** Ampule was charged with 4.03 g of monomer and 0.018 g of F-BPO initiator. After the mixture was degassed, the ampule was sealed. The polymerization was carried out at 50 °C for 5 days, and 3.82 g of polymer solid was obtained. For further purification, the prepared polymer was dissolved in hexafluorobenzene and then was precipitated in chloroform. After filtration, the solid was dried under vacuum at 60 °C for 1 day. The intrinsic viscosity of the polymer in hexafluorobenzene at 25 °C is 59 mL/g. The SEC number-average molecular weight is 8.0 × 10$^4$ and polydispersity 3.23.

**Preparation of Bis(2,2-difluoro-1-deuteriovinyl)difluoroformal (III) and Its Polymer (III-P). 2-Chloro-2,2-difluoro-1,1-dideuterioethanol.** A solution of 17.3 g (119.4 mmol) of methyl chlorodifluoroacetate in 200 mL of diethyl ether was added dropwise into the mixture of 5 g (119.4 mmol) of sodium borodeuteride, 100 mL of diethyl ether, and 1 mL of $CD_3OD$ with stirring. After stirring and refluxing for 3 h, the reaction mixture was cooled. 50 mL of 1 N hydrochloric acid aqueous solution was added, and the water layer was twice extracted with 100 mL of diethyl ether. The ether extracts and solution of 2-chloro-2,2-difluoro-1,1-dideuterioethanol were combined and dried over anhydrous magnesium sulfate. Rectification on a packed column yielded 11.4 g (96.1 mmol) of 2-chloro-2,2-difluoro-1,1-dideuterioethanol (bp 86−88 °C/760 Torr) a yield of 80.5%. $^1$H NMR: $\delta$ 3.10 (s, OH). $^{19}$F NMR: $\delta$ −65.1 (s, $-CF_2Cl$, 2F, $^3J_{H-F}$ = 11.0 Hz). $^{13}$C NMR: $\delta$ 127.7 (t, $^1J_{C-F}$ = 293.6 Hz), 66.0 (m, $-CD_2-$). Anal. Calcd for $C_2D_2HF_2ClO$: C, 20.24; Cl, 29.95. Found: C, 20.13; Cl, 29.40%.

**Bis(2-chloro-2,2-difluoro-1,1-dideuterioethyl)thionocarbonate**. To a solution of 28.0 g (236.0 mmol) of 2-chloro-2,2-difluoro-1,1-dideuterioethanol in 188 mL of water at 10 °C was added 24 mL of 10 N aqueous sodium hydroxide solutions. Then with vigorous stirring, a solution of 8.8 mL of thiophosgene (118.0 mmol) in 15 mL of $CH_2Cl_2$ was added dropwise over 20 min at 15 °C. Stirring was continued at room temperature for 3 h. The $CH_2Cl_2$ phase was separated and dried with $MgSO_4$. After solvent was removed, the residue was distilled to give 12.0 g (44.8 mmol, yield 38%) of product (bp 64−66 °C /11 Torr). $^{19}$F NMR: $\delta$ −62.1 (s, $-CF_2Cl$, 2F). $^{13}$C NMR: $\delta$ 72.8 (m, $-CD_2-$), 192.8(s, $-OCSO-$), 124.4 (t, $^1J_{C-F}$ = 293.0 Hz, $-CF_2Cl$). Anal. Calcd for $C_5D_4F_4Cl_2O_2S$: C, 21.51; Cl, 25.44. Found: C, 21.30; Cl, 25.16%.

**Bis(2-chloro-2,2-difluoro-1,1-dideuterioethyl)dichloroformal.** 12.0 g of gaseous chlorine was passed into a stirred solution of 10.2 g (36.5 mmol) of bis(2-chloro-2,2-difluoro-1,1-dideuterioethyl)thionocarbonate in 16 mL of $CH_2Cl_2$ for 6 h at room temperature. After filtering off a small amount of white precipitate, volatiles were removed under reduced pressure. The residual oil was distilled to give 10.1 g (33.2 mmol, yield 91%); bp 62−68 °C/12 Torr. $^{19}$F NMR: $\delta$ −62.4 (s, $-CF_2Cl$, 2F). $^{13}$C NMR: $\delta$ 70.6 (m, $-CD_2-$), 121.9 (s, $-OCCl_2O-$), 124.5 (t, $^1J_{C-F}$ = 292.5 Hz, $-CF_2Cl$). Anal. Calcd for$C_5D_4F_4Cl_4O_2$: C, 18.86; Cl, 44.65. Found: C, 18.75; Cl, 44.01%.

**Bis(2-chloro-2,2-difluoro-1,1-dideuterioethyl)difluoroformal.** Into a flamed flask under an argon atmosphere charged with 5.7 g (31.7 mmol) of $SbF_3$, 20 mL of $CH_3CN$, and 0.032 g of bromine, 10.1 g (31.7 mmol) of bis(2-chloro-2,2-difluoro-1,1-dideuterioethyl)dichloroformal was added dropwise at room temperature under constant stirring. After half an hour 30 mL of $CH_2Cl_2$ was added, and the reaction solution mixture was poured into water. The organic layer was washed with 30 mL of water, 30 mL of 1 N aqueous HCl solution, and 10 mL of brine and then dried onto anhydrous $MgSO_4$. Redistillation gave 7.5 g of pure bis(2-chloro-2,2-difluoro-1,1-dideuterioethyl)difluoroformal (bp 124−132 °C/760 Torr) in 83.2% yield. $^{19}$F NMR: $\delta$ −63.5 (s, 4F, $-CF_2Cl$), −64.0 (m, 2F, $-OCF_2O-$). $^{13}$C NMR: $\delta$ 65.7 (m, $-CD_2-$), 120.1 (t, $^1J_{C-F}$ = 254.6 Hz, $-OCF_2O-$), 122.6 (t, $^1J_{C-F}$ = 292.7 Hz, $-CF_2Cl$). Anal. Calcd for $C_5D_4F_6Cl_2O_2$: C, 21.05; Cl, 24.91. Found: C, 20.85; Cl, 24.50%.

**Bis(2,2-difluoro-1-deuteriovinyl)difluoroformal.** A mixture of bis(2-chloro-2,2-difluoroethyl)difluoroformal (7.5 g, 26.7 mmol), KOH (3.5 g, 53.4 mmol), and 2.6 mL of DMSO was refluxed. The liquid with bp of 60−62 °C/760 Torr was distilled out using a spinning band distillation apparatus, yielding 3.6 g (17.1 mmol) of bis(2,2-difluoro-1-deuteriovinyl)difluoroformal (yield 64%). $^{19}$F NMR: $\delta$ −65.4 (s, 2F, $-OCF_2O-$), −93.6 (m, F at vinyl and trans to D, 1F), −112.2 (m, F at vinyl and cis to D, 1F). $^{13}$C NMR: $\delta$ 155.3 (dd, $^1J_{C-F}$ = 293.0 Hz, $^1J_{C-F}$ = 280.9 Hz, $=CF_2$), 99.0 (ddt, $^2J_{C-F}$ = 60.8 Hz, $^2J_{C-F}$ = 15.5 Hz, $^4J_{C-F}$ = 3.9 Hz, $=CFO-$), 119.6 (tm, $^1J_{C-F}$ = 256.0 Hz, $-OCF_2O-$). IR: 1173 cm$^{-1}$ (C=C). MS, *m/e* 210 (M+).

**Polymerization of Bis(2,2-difluoro-1-deuteriovinyl)-difluoroformal.** In an ampule was added 1.84 g of monomer and 0.012 g of F-BPO initiator. After the mixture was degassed, the ampule was sealed. The polymerization was carried out at 50 °C for 5 days, and 1.61 g of polymer solid was obtained. For further purification, the polymer obtained was dissolved in hexafluorobenzene and participated into chloroform. After filtration, the solid polymer was dried in a vacuum at 60 °C for 1 day. The intrinsic viscosity of the polymer in hexafluorobenzene at 25 °C is 35 mL/g. The SEC number-average molecular weight is 4.2 × 10$^4$ and polydispersity 2.75.

## Results and Discussion

The $^{13}$C NMR spectrum of I showed that the signals of $F_2C=$ and $=CHO-$ are at 156.22 and 105.658 ppm, respectively, indicating that the double bonds are polarized. When the hydrogen atoms ($-OCH_2O-$) of this formal were substituted with two fluorine atoms as is the case of II, the $^{13}$C NMR spectrum signals of $F_2C=$ and $=CHO-$ groups were found to be at 155.39 and 98.96 ppm. The difference is larger relative to monomer I because of the stronger electron-withdrawing effect of $-OCF_2-$ group. Thus, free radical initiators react at the

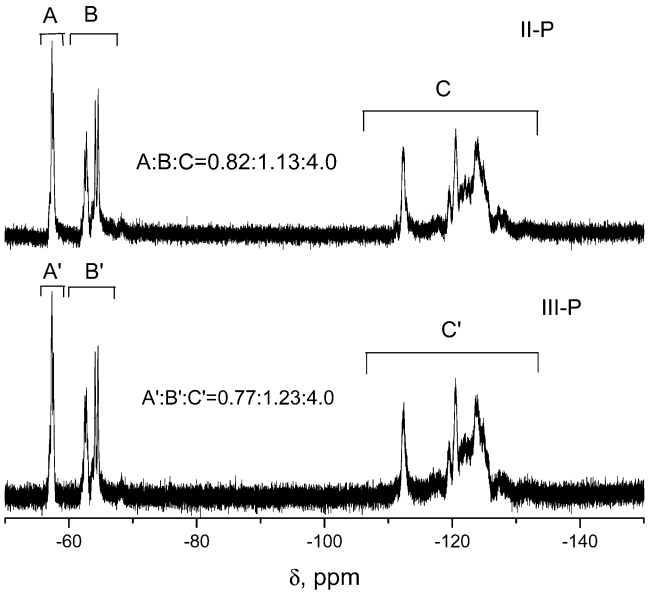
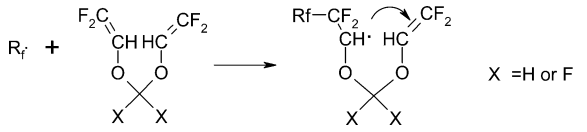



**Figure 2.** $^{19}$F NMR spectra of II-P and III-P ($d_8$-1,4-dioxane used as solvent).

**Scheme 2. Polymerization Propagation**




tail position of the double bond and form an electrophilic radical. The resulting radicals may have a favorable polar transition state and react with the adjacent nuclepohilic double bond. Thus, the cyclopolymerization is proceeding (Scheme 2).

The polymerization of these monomers was carried out in bulk. Since these monomers were not miscible with nonfluorinated free radical initiators such as 2,2′-azobis(2-methylpropionitrile) (AIBN) and benzoyl peroxide, perfluorobenzoyl peroxide was used instead. These monomers were polymerized smoothly at 50 °C with high conversions. It was observed that during bulk polymerization of monomers II and III polymerizations proceeded homogeneously throughout the polymerization, and transparent rods were directly obtained after polymerization. However, solid polymer deposited from reaction mixture of monomer I. Polymer 1-P from monomer I was insoluble in organic solvents such as THF, DMSO, DMF, 1,4-dioxane, benzene, hexafluorobenzene, 1,1,2-trichloro-1,2,2-trifluoroethane, trifluoroethanol, trifluoroacetic acid, and Fluorinert FC-75. This indicated that polymer I-P was probably crosslinked. However, polymers II-P and III-P were soluble not only in fluorinated solvents such as hexafluorobenzene and Fluorinert FC-75 but also in some nonfluorinated solvents such as THF, 1,4-dioxane, and DMF. The purified polymers did not show any absorptions corresponding to the vinyl group at 1173 cm$^{-1}$ in the IR spectra, and also no signals of fluorine atoms attached to the double bonds at −98 and −118 ppm in the $^{19}$F NMR spectrum were observed (Figure 2). These experimental observations indicated that there are no unreacted vinyl groups remaining in the polymers.

Figure 2 shows the $^{19}$F NMR spectra of II-P and III-P. The spectra of both polymers are similar. The signals at −55 and −60 ppm are attributed to the $-OCF_2O-$ group in the five-membered ring units and signals at

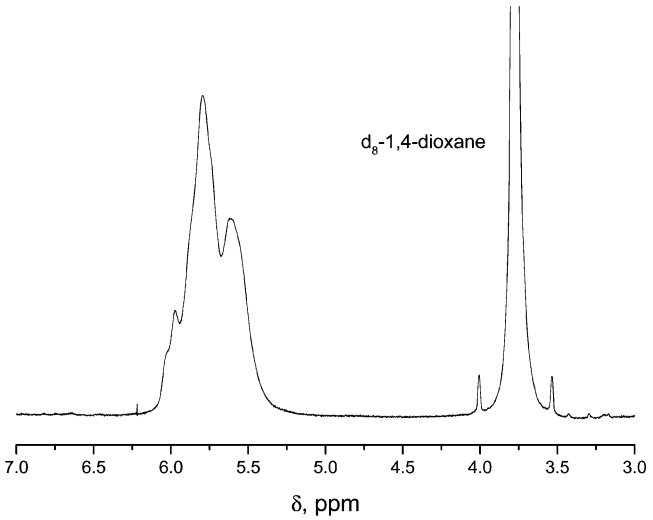



**Figure 3.** $^1$H NMR spectrum of II-P ($d_8$-1,4-dioxane used as solvent).

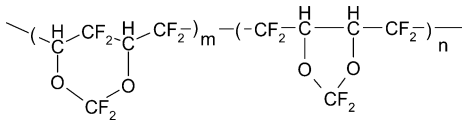


**Figure 4.** Chemical structure of II-P.

−60 to −67 ppm to $-OCF_2O-$ group in the six-membered ring. The peak group ranging from −110 to −130 ppm was assigned to the $-CF_2-$ groups of the polymer backbone. The ratio of five-membered to six-membered rings was evaluated from integrals corresponding to the aforementioned signals. The contents of five-membered rings in II-P and polymer II-P are nearly the same (41.0 and 38.5%, respectively). For II-P, the proton peaks corresponding to $-CHCH-$ in the five-membered rings and $-CHCF_2CH-$ from the six-membered rings are overlapped at 6.25−5.25 ppm (Figure 3). The chemical structure of II-P is illustrated in Figure 4. The coexistence of five- and six-membered rings in the polymer chain has also been observed in similar fluorinated cyclopolymers such as poly(perfluorobutenyl vinyl ether)[9] and partially hydrogen-substituted poly(perfluorobutenyl vinyl ether)[10] as well as other partially fluorinated polymers.[13]

The initial decomposition temperature (under $N_2$ atmosphere) of polymer I-P is 200 °C. However, polymers II-P and III-P have outstanding thermal stability, and the initial decomposition temperatures (under $N_2$ atmosphere) are higher than 400 °C. Polymer I-P has a glass transition temperatures of 122 °C and polymers II-P and III-P around105 °C, as depicted in Figure 5. Furthermore, they do not exhibit a melting endotherm, indicating that they are amorphous.

The dependence of the dielectric constant of polymer II on frequency is illustrated in Figure 6. It varies between 1.98 and 1.82 when the frequency ranges from 0.1 to $3 \times 10^6$ Hz. Compared with the dielectric constant of Cytop and Teflon PTFE ($\epsilon = 2.1-2.2$), polymer II shows much lower values.[10d]

The films (0.22 mm thickness) of polymers II-P and III-P obtained by casting were flexible and free-standing. They have outstanding optical clarity ranging from visuable to near-IR region, as shown in Figure 7. In comparison with the hydrogen-containing polymer II-P, the deuterated polymer III-P was found to be only slightly different in optical transmittance.

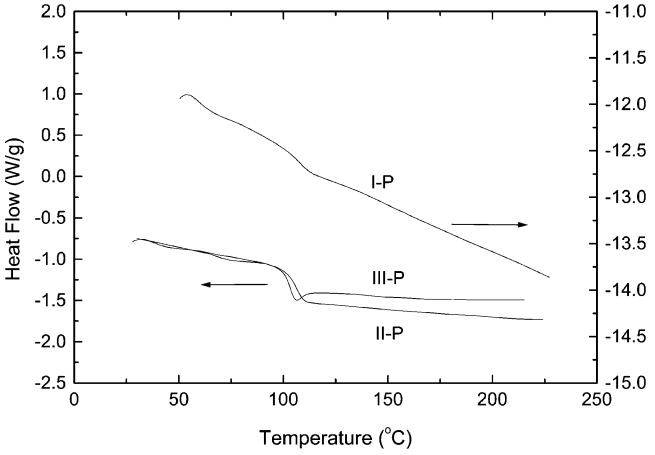



**Figure 5.** DSC trace of I-P, II-P, and III-P (heating rate 20 °C/min).

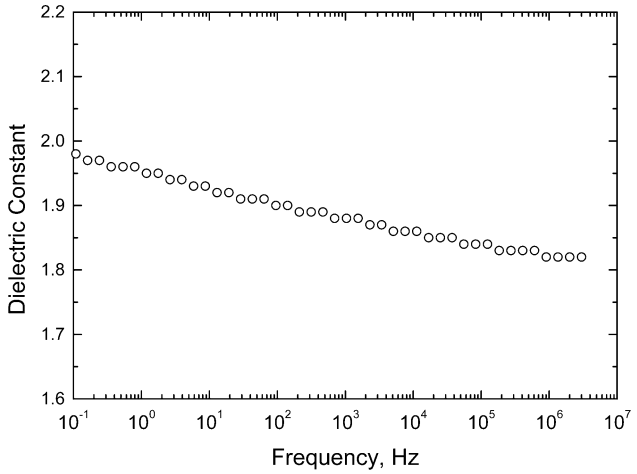



**Figure 6.** Dependence of dielectric constant of II-P on frequency at 25 °C.

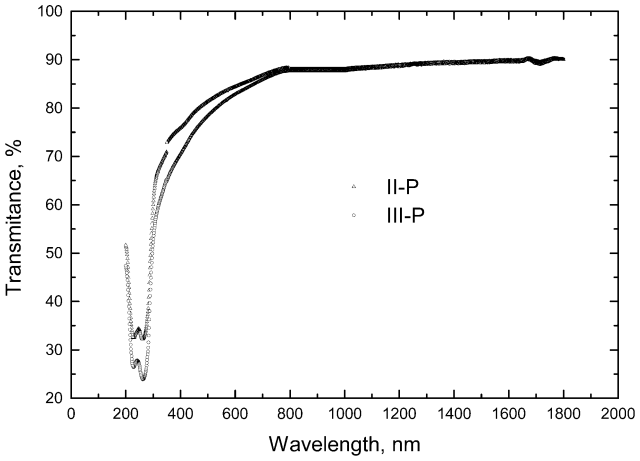



**Figure 7.** Transmittance spectra of II-P and III-P (film thickness 0.22 mm).

For plastic optical fiber communications, the bandwidth is strongly related to the material dispersion, and the lower the material dispersion, the higher the bandwidth. Recently, Asahi Glass Co. of Japan successfully developed and commercialized the perfluorinated polymer, poly(perfluorobutenyl vinyl ether) (CYTOP), as a plastic optical fiber core material. This polymer is completely amorphous and has a much lower material dispersion than silica and PMMA. The refractive indices of II-P and III-P were measured at various wavelengths,

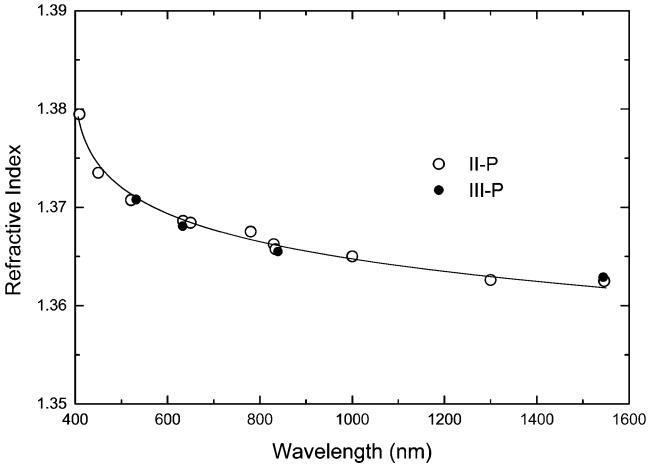



**Figure 8.** Dependence of the refractive index on wavelength for polymers II-P and III-P.

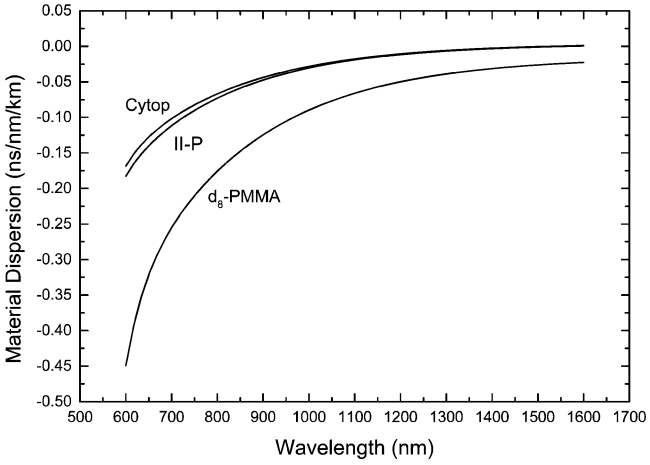



**Figure 9.** Comparison of material dispersion of polymer II-P, Cytop, and $d_8$-PMMA.

and it was found that they are nearly the same for both polymers (Figure 8). The material dispersion $M(\lambda)$ was estimated by using the data in Figure 8 based on eq 1[11]

$$M(\lambda) = -\frac{\lambda}{c}\frac{\mathrm{d}^2 n}{\mathrm{d}\lambda^2} \qquad (1)$$

where $n$ is the refractive index of the material, $\lambda$ is the wavelength of interest, and $c$ is the velocity of light in vacuo. The refractive index data as a function of wavelength were fit to a three-term Sellmeier equation to calculate $\mathrm{d}^2n/\mathrm{d}\lambda^2$. The material dispersion of polymer II estimated by the above equation is shown in Figure 9 along with perfluoro-polymer Cytop and perdeuterated PMMA. Though II-P contains two hydrogen atoms in every monomer unit, the material dispersion was found to be comparable to the perfluorinated polymer CYTOP and much lower than perdeuterio-PMMA.

**Acknowledgment.** The authors thank Dr. T. Ishigure of Keio University for his kind help with the measurement of material dispersion. The work was supported by the Japan Science and Technology Corp. through the Grant for ERATO Photonic Polymer.

## References and Notes

(1) Emslie, C. *J. Mater. Sci.* **1988**, *23*, 2281.

(2) White, W. R.; Blyler Jr., L. L.; Glaretla, G.; Quan, X.; Reed, W. A.; Duesser, M.; Sherehuk, G. J.; Wiltzius, P. *Prod. Boston Conf. OPF* **2000**, *6*.
(3) Nakamura, S.; Seoh, M.; Lwasa, N.; Nagahama, S. *Jpn. J. Appl. Phys.* **1995**, *34*, L797.
(4) Kaino, T.; Fujik, M.; Jinguji, K. *Rev. Electron Commun. Lab*, **1984**, *32*, 478.
(5) Grob, W. *Makromol Chem.* **1988**, *1989*, 2861.
(6) Koike, Y.; Ishigure, T. *Proc., 23rd European Conf. OPT Commun., Edinburgh, Scotland* **1997**, *59*.
(7) Nihei, E.; Ishigure, T.; Koike, Y. *Appl. Opt.* **1996**, *35*, 7085.
(8) Ishigure, T.; Nihei, E.; Koike, Y.; Forbes, C. E.; Laniove, L.; Straff, R.; Deckers, H. A. *IEEE, Photonics Technol. Lett.* **1995**, *7*, 403.
(9) Onishi, T. *Fiber Preprint, Soc. Fiber, Kyoto Univ*. June 2000.
(10) (a) Yang, Z.-Y.; Feming, A. E.; Smart, B. E. *J. Am. Chem. Soc.* **1994**, *116*, 4135. (b) Yang, Z.-Y. USA Patent 5336741. (c) Hung, M.-H.; Resnick, P. R.; Smart, B. E.; Buck, W. H. *Polym. Mater. Encycl.* **1996**, *4*, 2466. (d) Smart, B. E.; Feiring, A. E.; Krespan, C. G.; Yang, Z.-Y.; Hung, M.-H.; Resnick, P. R. *Macromol. Symp.* **1995**, *98*, 753.
(11) Feming, J. W. *J. Am. Ceram. Soc.* **1976**, *59*, 503.
(12) (a) Aso, C.; Kunitake, T.; Ando, S. *J. Macromol. Sci., Chem.* **1971**, *A5* (1), 167−180. (b) Minoura, Y.; Mitoh, M. *J. Polym. Sci., Part A* **1965**, *3*, 2149. (c) Tsukino, M.; Kunitake, T. *Polym. J.* **1979**, *11*, 437. (d) Tsukino, M.; Kunitake, T. *Polym. J.* **1985**, *17*, 943. (e) Dietrich, H. J.; Raymond, M. A. *J. Macromol. Sci., Chem.* **1972**, *A6*. 191.
(13) Dolbier Jr., W. R.; Rong, X. X.; Bartberger, M. D.; Koroniak, H.; Smart, B. E.; Yang, Z.-Y. *J. Chem. Soc., Perkin Trans.* **1998**, *2*, 219.
(14) Belf, L.; Buxton, M.; Fuller, G. *J. Chem. Soc.* (*London*) **1965**, 3372.
(15) Sugiyama, N. European Patent 0950672.

MA049462D