Synthesis and Radical Polymerization of Perfluoro-2-methylene-1,3-dioxolanes

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ABSTRACT: A new efficient synthetic route was developed for perfluorinated 2-methylene-1,3-dioxolane monomers via a direct fluorination of the hydrocarbon precursors prepared from methyl pyruvate and diols. Perfluoro-2-methylene-4,5-dimethyl-1,3-dioxolane (PMDD) and perfluoro-3-methylene-2,4-dioxabicyclo-[4.3.0]nonane (PMDN) were thus synthesized via this new method, among which PMDN is first reported. The radical polymerizations of those monomers were performed under various conditions. The kinetic results indicated that polymerization rate of PMDD is higher than that of PMDN. Oxygen did not affect the polymerization yield but strongly affected the polymer structure. The polymerization in the presence of oxygen produced a polymer containing unstable units. Hydrogen-containing solvents result in a lower molecular weight polymer. 2,2′-Azobis(isobutyronitrile) cannot initiate the polymerization in a perfluoro solvent or in bulk. Also, photopolymerizations of those monomers were performed in the presence of carbon tetrabromide or carbon tetrachloride, and the mechanism is discussed. The polymer of PMDD has a glass transition temperature at 155 °C, and the polymer of PMDN has a glass transition temperature at 161 °C. These polymers with high glass transition temperature, low refractive index, low material dispersion, and extraordinary optical transmission from the deep ultraviolet to near-infrared regions may be used as optical fibers, pellicles, or antireflective coating materials.

Introduction

Fluorinated polymers have become of increasing interest in the development of advanced materials having superior thermal and chemical stability, excellent electrical insulating ability, and unique optical properties.[1−3] Especially, perfluorinated polymer has been applied in graded-index polymer optical fibers (GI POF) for short−medium haul data communication in order to obtain excellent low attenuation loss in the near-infrared region and high bandwidth due to the performance of the perfluorinated polymer compared to the poly(methyl methacrylate) (PMMA)-based plastic optical fiber.[4] Currently, an interfacial gel polymerization is utilized to prepare GI-POF preform. This important method requires a radically polymerizable monomer. And also, POF requires that polymeric materials are amorphous and have relatively higher glass transition temperature (T_g) for high-temperature working conditions. Therefore, we are currently searching for a new perfluorinated monomer which can afford amorphous perfluoropolymers with a higher T_g through radical homo- or copolymerization.

Compared to a large number of radically polymerizable hydrocarbon monomers, only a few classes of perfluoromonomers can homopolymerize under normal conditions via the free radical mechanism. The most typical example of a perfluoromonomer polymerized via the free radical mechanism and developed by DuPont in 1937 is tetrafluoroethylene.[5] Gradually, perfluoro-2-methylene-1,3-dioxolanes, perfluorodihydrodioxins, and perfluorodioxoles were also developed by DuPont.[2,3] In addition, perfluorodienes as a new class of monomer have been developed by Asahi Glass for producing amorphous perfluoropolymers since 1989.[2,3,6] Regarding the class of perfluoro-2-methylene-1,3-dioxolanes, only two monomers were reported. The first example in the class is perfluoro-2-methylene-4-methyl-1,3-dioxolane (PMMD), which was developed by DuPont in 1967 via perfluoropyruvyl fluoride prepared from hexafluoropropylene epoxide.[7] Using a similar method, perfluoro-2-methylene-4,5-dimethyl-1,3-dioxolane (PMDD) was developed by Asahi Glass in 1993.[8] The methods for their preparations were complicated and costly. Recently, PMMD was prepared from partially fluorinated ester by liquid-phase direct fluorination.[9] However, this method still requires the use of expensive fluorinated starting materials: perfluoroacyl fluoride. In this work, we report a new and efficient method for the preparation of this class of monomers. The polymerization behavior of the resulting monomers was investigated. The properties of the resulting polymers were investigated as well.

Experimental Section

Materials. 2,3-Butanediol (mixture of stereoisomers, 98%), Dowex 50WX8-100 ion-exchange resin, and absolute benzene were purchased from the Aldrich Chemical Co. Methyl pyruvate (97%) and 1,2-cyclohexanediol (*cis*- and *trans*- mixture, 98%) were purchased from TCI. Hexafluorobenzene (99%) and hexafluoro-2-propanol (HFIP) (99%) were purchased from SynQuest Fluorochemical Laboratory. Fluorinert FC-75 (a perfluorinated solvent) was obtained from 3M Co. All reagents were used without further purification. Perfluorobenzoyl peroxide (F-BPO) was prepared from pentafluorobenzoyl chloride and hydrogen peroxide according to a published method.[10] The crude initiator was recrystallized from hexane, and the purified initiator has a melting point of 76−78 °C; its half-lives were calculated to be 25.6 and 2.6 h at 60 and 80 °C, respectively, based on the reported decomposition rate constant in benzene.[11] 2,2′-Azobis(isobutyronitrile) (AIBN) (Aldrich, 98%) was purified by recrystallization from methanol.

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Instrumentation. The ^{1}H (300 MHz) and ^{19}F (282 MHz) NMR spectra were obtained on a Bruker ACF 300 spectrometer. NMR spectra for these perfluoropolymers were measured in hexafluorobenzene with deuterated chloroform as an internal locking solvent at 50 °C. FTIR spectra were obtained with a Perkin-Elmer FTIR-1600 spectrometer. GC-MS measurements were conducted using an HP 5890 gas chromatograph and an HP 5970B mass spectrograph. Elemental analyses were performed at Complete Analysis Laboratories Inc., Parsippany, NJ. Viscosities of the solvent and filtered polymer solutions were measured using a modified Ubbelohde viscometer at 25 ± 0.05 °C in a thermostated bath. The intrinsic viscosity was evaluated using the Huggins equation. The differential scanning calorimetry (DSC) measurement was performed on a DSC 2920 module in conjunction with the TA Instruments 5100 system at a heating rate of 10 °C/min under a nitrogen atmosphere. The instrument was calibrated using indium and zinc as calibration standards for the temperature and enthalpy changes. The midpoint of the heat capacity transition was taken as the glass transition temperature (T_g). Thermogravimetric analysis (TGA) was performed on Hi-Res Modulated TGA2950 thermogravimetric analyzer under nitrogen at a heating rate of 10 °C/min. The refractive index of the film was obtained with a Metricon model 2010 prism coupler. The transmission spectrum was recorded with a Cary 6000i UV−vis−NIR spectrophotometer.

Synthesis of PMDD. Synthesis of Methyl 2,4,5-Trimethyl-1,3-dioxolane-2-carboxylate. The reaction mixture of the 2,3-butanediol (180 g, 2.0 mol), methyl pyruvate (204 g, 2.0 mol), cation-exchange resin (H form) (10 g), and absolute benzene (1 L) was refluxed until the evolution of water ceased in a flask fitted with a Dean−Stark trap. The reaction was kept for 2 days. After solvent was removed, the residue was distilled to give 192 g (1.1 mol) of product. Yield 55%; bp 45 °C/1.0 mmHg. ^{1}H NMR ($CDCl_3$) δ (ppm): 1.15 (d, 6H, $-CH_3$), 1.50 (s, 3H, $-CH_3$), 3.80 (s, 3H, OCH_3), 4.2−4.4 (m, 2H, −OCH−). Anal. Calcd for $C_8H_{14}O_4$: C, 55.16; H, 8.10. Found: C, 55.04; H, 8.15.

Synthesis of Perfluoro-2,4,5-trimethyl-1,3-dioxolane-2-carboxylic Acid. The methyl 2,4,5-trimethyl-1,3-dioxolane-2-carboxylate (500 g, 2.87 mol) was fluorinated with fluorine gas diluted with nitrogen in Fluorinert FC-75. The liquid-phase fluorination was carried out in cooperation with Exfluor Research Co. (Round Rock, TX). After flushing the system using nitrogen gas for 1.0 h, fluorine gas diluted to 20% with nitrogen gas was blown into the reaction mixture at a flow rate of 240.0 L/h at ambient temperature (∼25 °C). The reaction was performed over about 20 h, and the reaction temperature was controlled around 25 °C. After the reaction stopped, the mixture was neutralized with aqueous KOH solution (5 N, 1100 mL). The aqueous phase was separated, and the water was removed. The solid was treated with an excess of concentrated HCl (800 mL), and the organic phase was obtained; the acid was obtained by distillation. Yield (925 g, 2.58 mol) 90%; bp 61 °C/2.5 mmHg. ^{1}H NMR ($CDCl_3$) δ (ppm): 9.4 ppm (s, 1H, COOH). ^{19}F NMR ($CDCl_3$) δ (ppm): trans and cis isomers, major/minor: 2.67/1.00 (mol/mol); −79.29 and −79.63 (minor), −79.32 and −79.36 (major) (d, 6F in total, $-CF_3$), −80.81 and −80.93 (minor), −81.11 and −81.14 (major) (d, 3F in total, $-CF_3$), −120.8 (minor), −124.6 and −125.6 (major) (m, 2F in total, −OCF−).

Synthesis of Perfluoro-2-methylene-4,5-dimethyl-1,3-dioxolane. The perfluoro-2,4,5-trimethyl-1,3-dioxolane-2-carboxylic acid (100 g, 0.28 mol) was converted to potassium salt by neutralization with aqueous KOH (2 N, 140 mL). The salt was dried at 50 °C under vacuum for 1 day. The salt was decomposed at 250 °C for 2 h to yield the product, which was collected in a trap cooled to −78 °C. The product was purified by distillation using a spinning band distillation apparatus to give 64 g (0.22 mol) of the monomer. Yield 78%; bp 60 °C (lit. 63 °C[8]). ^{1}H NMR ($CDCl_3$) δ (ppm): none. ^{19}F NMR ($CDCl_3$) δ (ppm): trans and cis isomers, major/minor: 2.67/1.00 (mol/mol); −80.35 (s, $-CF_3$ of major isomer) and −81.09 (s, $-CF_3$ of minor isomer) (6F in total, $-CF_3$), −126.61 (t, $=CF_2$ of major isomer) and −126.88 (t, $=CF_2$ of minor isomer) (2F in total, $=CF_2$), −129.49 (m, −OCF− of major isomer) and −129.84 (m, −OCF− of minor isomer) (2F in total, −OCF−). GC-MS: *m/e* 294 (M^+), 275 (M^+-F), 225 (M^+-CF_3), 200 (M^+-CF_2COO: $C_4F_8^+$), 181 ($C_4F_7^+$), 150 ($CF_3CF{=}CF_2^+$), 131 ($CF_2{=}CFCF_2^+$), 100 ($C_2F_4^+$), 78 ($CF_2{=}C{=}O^+$), 69 (CF_3^+), and 50 (CF_2^+).

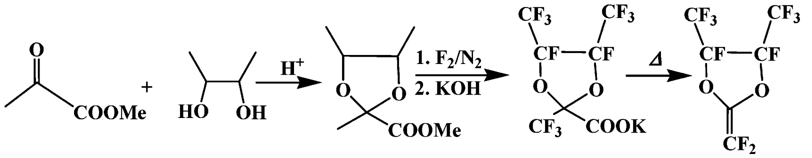
Synthesis of Perfluoro-3-methylene-2,4-dioxabicyclo-[4.3.0]nonane (PMDN). Synthesis of Methyl 3-Methyl-2,4-dioxabicyclo[4.3.0]nonane-3-carboxylate. The reaction mixture of the 1,2-cyclohexanediol (232 g, 2.0 mol), methyl pyruvate (204 g, 2.0 mol), cation-exchange resin (H form) (10 g), and absolute benzene (1 L) was refluxed until the evolution of water ceased in a flask fitted with a Dean−Stark trap. The reaction was kept for 3 days. After solvent was removed, the residue was distilled to give 232 g (1.16 mol) of product. Yield 58%; bp 60 °C/0.3 mmHg. ^{1}H NMR ($CDCl_3$) δ (ppm): 1.52 (s, 3H, CH_3), 1.2−1.9 (m, 8H, $-CH_2-$), 3.8 (s, 3H, $-OCH_3$), 4.2 (m, 2H, −OCH−). Anal. Calcd for $C_8H_{14}O_4$: C, 59.98; H, 8.05. Found: C, 59.56; H, 8.11.

Synthesis of Perfluoro-3-methyl-2,4-dioxabicyclo[4.3.0]-nonane-3-carboxylic Acid. The methyl 3-methyl-2,4-dioxabicyclo[4.3.0]nonane-3-carboxylate (666 g, 3.33 mol) was fluorinated with fluorine gas diluted with nitrogen in Fluorinert FC-75. The fluorination was performed at Exfluor (Round Rock, TX) as mentioned above. After flushing the system using nitrogen gas for 1.0 h, fluorine gas diluted to 20% with nitrogen gas was blown into the reaction mixture at a flow rate of 240.0 L/h at ambient temperature (∼25 °C). The reaction was performed over about 26 h, and the reaction temperature was controlled around 25 °C. After the reaction stopped, the mixture was treated with aqueous KOH solution (5 N, 1300 mL) to form organic and water phases. The water phase was separated, and the water was removed. The solid was treated with concentrated HCl (900 mL), and the organic phase was obtained; the acid was obtained by distillation. Yield (1317 g, 3.14 mol) 94%; bp 78 °C/1.0 mmHg. ^{1}H NMR ($CDCl_3$) δ (ppm): 8.5 (s, 1H, COOH)). ^{19}F NMR ($CDCl_3$) δ (ppm): −79.6 (t, 3F, $-CF_3$), −122−131 (m, 10F, −OCF− and $-CF_2-$).

Synthesis of Perfluoro-3-methylene-2,4-dioxabicyclo-[4.3.0]nonane. The perfluoro-3-methyl-2,4-dioxabicyclo[4.3.0]-nonane-3-carboxylic acid (100 g, 0.24 mol) was converted to potassium salt by neutralization with aqueous KOH (2 N, 120 mL). The salt was dried at 50 °C under vacuum for 1 day. The salt was decomposed at 250 °C for 2 h to yield the product which was collected in a trap cooled to −78 °C. The product was purified by distillation using a spinning band distillation apparatus to give 71 g (0.20 mol) of the monomer. Yield 84%; bp 99 °C. ^{1}H NMR ($CDCl_3$) δ (ppm): none. ^{19}F NMR ($CDCl_3$) δ (ppm): −126.84 (t, 2F, $=CF_2$), −127.98, −128.98, −129.29, −130.28, −131.66, −132.67, −133.62 and −134.62 (8F, $-CF_2-$ in the cyclohexyl group), −138.25 (s, 2F, −OCF−). GC-MS: *m/e* 356 (M^+), 337 (M^+-F), 262 (M^+-CF_2COO: $C_6F_{10}^+$), 243 ($C_6F_9^+$), 212 ($C_5F_8^+$), 193 ($C_5F_7^+$), 162 ($C_4F_6^+$), 143 ($C_4F_5^+$), 131 ($CF_2{=}CFCF_2^+$), 100($C_2F_4^+$), 93 ($FC{\equiv}CCF_2^+$), 78 ($CF_2{=}C{=}O^+$), 69 (CF_3^+), and 50 (CF_2^+).

Polymerization. PMDD Polymerization. The PMDD (1.69 g, 5.75 mmol), F-BPO (13.0 mg, 0.031 mmol), and hexafluorobenzene (0.5 mL) were charged in the glass tube, which was then degassed and refilled with argon in three vacuum−freeze−thaw cycles. The tube was then sealed and heated at 60 °C for 24 h. The resulting polymer (1.50 g, 88%) was precipitated from hexafluorobenzene solution into chloroform, isolated using a centrifuge, and dried under vacuum at 50 °C. The intrinsic viscosity of the sample in hexafluorobenzene at 25 °C is 11.0 mL/g. The bulk polymerization was carried out in a similar way. The solid product was dissolved in hexafluorobenzene and then was precipitated in chloroform. The polymerization under air atmosphere was performed in a glass tube equipped with a three-way stopcock which was closed without degassing. The photopolymerization was also performed in the presence of carbon tetrabromide or carbon tetrachloride. The monomer and additive were charged in a glass tube, which was also then treated in three vacuum−freeze−thaw cycles and sealed. The glass tube was irradiated by UV light at about 365 nm.

Scheme 1. Synthesis of Perfluoro-2-methylene-4,5-dimethyl-1,3-dioxolane



Scheme 2. Synthesis of Perfluoro-3-methylene-2,4-dioxabicyclo[4.3.0]nonane

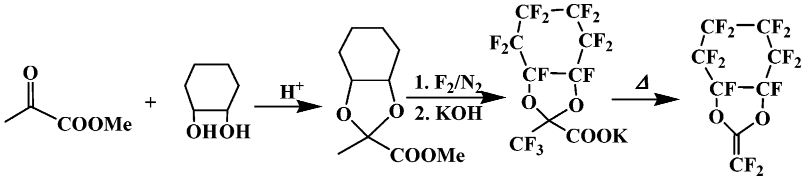


Table 1. Radical Polymerization of Perfluororo-2-methylene-1,3-dioxolanes[a]

run	monomer	additive	solvent	$[M]_0$	atmosphere	time (h)	yield[b]	intrinsic viscosity (mL/g)[c]
1	PMDD	F-BPO	none	5.75	Ar	48	95	24.4
2	PMDN	F-BPO	none	5.00	Ar	96	74	9.6
3	PMDD	F-BPO	C_6F_6	3.85	Ar	24	88	11.0
4	PMDD	AIBN	C_6F_6	3.85	Ar	24	trace	
5	PMDD	F-BPO	C_6F_6	3.85	air	24	85	7.5
6	PMDD	F-BPO	$C_6F_6/CHCl_3$ (v/v, 1/1)	1.92	Ar	24	87	3.1
7	PMDD	AIBN	$C_6F_6/CHCl_3$ (v/v, 1/1)	1.92	Ar	24	13	4.7
8	PMDD	F-BPO	HFIP	1.92	Ar	24	89	7.8
9	PMDD	AIBN	HFIP	1.92	Ar	24	trace	
10	PMDN	F-BPO	C_6F_6	3.33	Ar	96	46	3.4
11	PMDN	F-BPO	C_6F_6	3.33	air	96	35	3.0
12	PMDN	F-BPO	HFIP	1.67	Ar	24	20	2.6

[a] $[\text{Initiator}]_0 = 0.02$ M; temperature: 60 °C; PMDD: perfluoro-2-methylene-4,5-dimethyl-1,3-dioxolane; PMDN: perfluoro-3-methylene-2,4-dioxabicyclo[4.3.0]nonane. [b] Precipitated into chloroform. [c] In hexafluorobenzene solution at 25 °C.

PMDN Polymerization. The PMDN (1.78 g, 5.0 mmol), F-BPO (13.0 mg, 0.031 mmol), and hexafluorobenzene (0.5 mL) were charged in the glass tube, which was then degassed and refilled with argon in three vacuum−freeze−thaw cycles. The tube was then sealed and heated at 60 °C for 96 h. The resulting polymer (0.82 g, 46%) was precipitated from hexafluorobenzene solution into chloroform, isolated using a centrifuge, and dried under vacuum at 50 °C. The intrinsic viscosity of the sample in hexafluorobenzene at 25 °C is 3.4 mL/g. Other polymerizations of PMDN were performed with the methods similar to PMDD polymerizations.

Results and Discussion

Monomer Synthesis. As shown in Schemes 1 and 2, the first step for the synthetic route is to synthesize the hydrocarbon dioxolane derivatives. The methyl pyruvate and diols were used as starting materials since they are commercially available and quite cheap. A dilute benzene solution and slightly reduced pressure were adopted to reduce the side reaction such as condensation polymerization. Even so, the polymer was still produced in about 30% yield as a main side product. Hence, the yield in this step was moderate. Similarly, the dioxolane derivatives have been prepareed from pyruvic acid in a yield about 50%.[12]

The second step for the synthetic route is liquid-phase direct fluorination developed by Lagow.[13] Direct fluorination of a hydrocarbon ester such as octanoyl acetate has been reported to afford two kinds of perfluorinated acids in a high yield.[13] The dioxolane derivatives bearing a fluorinated ester have also reported to be fluorinated in good yield.[9] However, the dioxolane derivatives without fluorinated moiety have not been studied using the direct fluorination method. The direct fluorination on the hydrocarbon analogues of dioxolanes in a perfluorinated solvent afforded a yield over 90% in all cases. This means the ring-opening of the dioxolane ring did not occur during fluorination in the perfluorinated solvent at ambient temperature (~25 °C). After fluorination aqueous KOH solution was added to hydrolyze the perfluorinated ester. The potassium salt was obtained from the aqueous phase. The salt can be converted into perfluorinated acid by acidification.

The third step for the synthetic route is the thermal elimination of the obtained perfluorinated potassium salt to produce the corresponding monomers. This is a widely used method to produce perfluorinated vinyl monomers in fluorine chemistry.[14] The yield is generally high as we reported here.

By using the above protocol, dozens of perfluoromonomers could be readily designed and synthesized from methyl pyruvate and diols. This method was first proved to be feasible by synthesizing a known monomer, PMDD, which was already reported to be prepared by other method.[8] Then, to broaden the utilization of this method, we designed a new monomer with a bulky cyclohexyl group which was expected to enhance the glass transition temperature of the polymer. As expected, perfluoro-3-methylene-2,4-dioxabicyclo[4.3.0]-nonane was successfully synthesized with this method as reported in the experimental part. In addition, this method could be applied for the preparation of a new class of monomer: perfluoro-2-methylene-1,3-dioxanes. We recently synthesized perfluoro-2-methylene-1,3-dioxane by this method after the above two monomer's preparation and published as part of work to compare the polymerization reactivity of dioxolane and dioxane derivatives.[15]

Polymerization. The radical polymerizations of the two monomers were performed under various conditions. The results are summarized and listed in Table

Table 2. Photopolymerization of Perfluoro-2-methylene-1,3-dioxolanes[a]

run	monomer	additive	solvent	$[M]_0$	temp (°C)	time (h)	yield[b]	intrinsic viscosity (mL/g)[c]
1	PMDD	CBr_4	none	5.75	25	48	88	10.8
2	PMDN	CBr_4	none	5.00	50	96	74	5.6
3	PMDD	none	none	5.75	25	24	trace	
4	PMDD	CBr_4	C_6F_6	3.85	25	11	71	3.6
5	PMDD	CCl_4	none	5.75	25	24	85	13.3
6	PMDN	CCl_4	none	5.00	50	48	78	8.0

[a] Additive: 0.1 mol % for runs 1, 2, 5, and 6; 2.0 mol % for run 4; PMDD: perfluoro-2-methylene-4,5-dimethyl-1,3-dioxolane; PMDN: perfluoro-3-methylene-2,4-dioxabicyclo[4.3.0]nonane. [b] Precipitated into chloroform. [c] In hexafluorobenzene solution at 25 °C.

1. The bulk polymerization of PMDD was carried out using F-BPO as an initiator at 60 °C for 48 h to afford a transparent resin. Similarly, the bulk polymerization of PMDN at 60 °C for 96 h also afforded a transparent resin. After the products were purified by reprecipitation from hexafluorobenzene into chloroform, the yield is lower in the case of PMDN.

The solution polymerization was performed in hexafluorobenzene, hexafluoro-2-propanol and a mixed solvent of hexafluorobenzene and chloroform. The PMDD produces polymer in a high yield with a fluorinated initiator, but the polymerization gives only a trace of polymer at 60 °C for 24 h in fluorinated solvents (runs 4 and 9 in Table 1) with a nonfluorinated initiator, AIBN. This may be due to the fact that nonfluorinated radical species are not miscible with the fluorinated monomer. The fluorinated solvents surround the initial radicals to form a cage which retards the initiation. To understand the cage effect, an experiment was performed introducing a part of chloroform into the polymerization system. The polymer was thus obtained in an increased yield of 13% (run 7 in Table 1). This may suggest that the cage effect by perfluorinated solvents was loosened in the presence of chloroform. On the other hand, this may also due to the fact that the AIBN initial radical abstracts a hydrogen atom from chloroform to produce a trichloromethyl radical which may directly attack the fluoromonomer. It is reasonable because this kind of reaction has been applied in synthesizing CCl_3-terminated vinylidene fluoride telomers for preparation of block copolymers using atom transfer radical polymerization.[16]

Solution polymerization of PMDD in C_6F_6/$CHCl_3$ and HFIP with F-BPO as an initiator also afford the polymer in a high yield at 60 °C for 24 h (runs 6 and 8 in Table 1). In the mixed solvent of hexafluorobenzene and chloroform, it was observed that polymer precipitated out during polymerization. In HFIP, the resulting polymer is gellike during polymerization. The intrinsic viscosities of the obtained polymers in HFIP and C_6F_6/$CHCl_3$ are lower than that in hexafluorobenzene. It was thought that the chain transfer readily occurred by the growing fluorinated radical species abstracting a proton from the solvent. This may contribute to make the molecular weight lower than that in hexafluorobenzene.

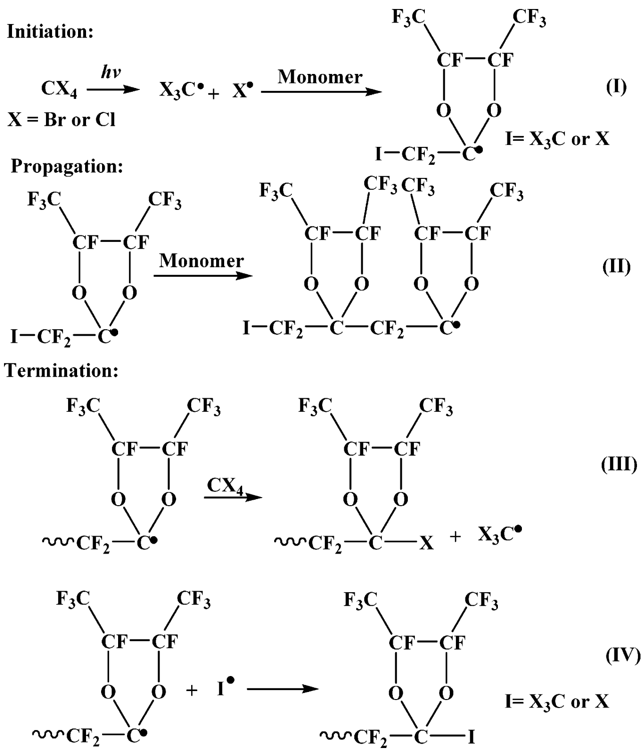
Solution polymerizations of PMDN in hexafluorobenzene and HFIP afford solid polymers (runs 10 and 12 in Table 1). Similarly, the intrinsic viscosity of the obtained polymer in HFIP is lower than that in hexafluorobenzene. It was also ascribed to the chain transfer reaction.

Compared with the experiment runs 3, 5, 10, and 11, it is interesting to note that the polymerization in the presence of air also affords polymers in a yield similar to that in an argon atmosphere. The detailed mechanism is discussed below. Unlike perfluoroalkanoyl peroxides, F-BPO produces pentafluorobenzoyloxy radical as the main primary initiating radical at 60 °C.[11,17] Therefore, the polymers obtained by using F-BPO as an initiator contain a weakly bonded pentafluorobenzoyl end group which was easily hydrolyzed by moisture, resulting in opacity of the polymer rod. To avoid the pentafluorobenzoyl end group, the photopolymerization was carried out under various conditions. The bulk photopolymerization of PMDD performed by UV irradiation at about 365 nm at 25 °C for 24 h in the presence of carbon tetrabromide or carbon tetrachloride produced more than 80% of polymer (runs 1 and 5 in Table 2). However, as a control experiment, the photopolymerization in the absence of carbon tetrabromide or carbon tetrachloride produced only trace of polymer (run 3 in Table 2). This indicates that the initial radicals were produced by breaking the C−Br or C−Cl bond. Solution photopolymerization was performed in hexafluorobenzene in the presence of carbon tetrabromide or carbon tetrachloride under an argon atmosphere, and the yield was over 70% after 11 h (run 4 in Table 2). The resulting polymers are soluble in fluorinated solvents such as hexafluorobenzene and Fluorinert FC-75. The viscosity was measured in a hexafluorobenzene solution. It is found that the molecular weight of the polymer obtained in the presence of carbon tetrabromide is lower than that in the presence of carbon tetrachloride (runs 1 and 5 in Table 2). Both molecular weights of the polymer obtained in the presence of carbon tetrabromide and carbon tetrachloride are lower than that of the polymer obtained by bulk polymerization using F-BPO as an initiator without additives. It is reasonable that carbon tetrabromide with a higher chain transfer constant led to a lower molecular weight during polymerization.

The bulk photopolymerization of PMDN was also performed in the presence of carbon tetrabromide and carbon tetrachloride (runs 2 and 6 in Table 2). Similarly, but it required a longer time and a higher polymerization temperature to obtain a higher yield. The molecular weight is also lower when carbon tetrabromide was used as an additive. The possible mechanism is illustrated in Scheme 3. The initiation was related to the C−Br or C−Cl bond breaking upon irradiation. The resultant radicals attack the active carbon−carbon double bond at the tail position to produce the initial monomer radical species. The second step is the initial radical species attack another monomer to propagate. The termination step may relate to the chain transfer to the carbon tetrabromide or carbon tetrachloride. Another possible termination is the coupling of two growing radicals.

The photopolymerizations of the two monomers afford fluorinated polymers with tribromomethyl or trichloromethyl end groups. Therefore, block copolymers with nonfluorinated monomers such as styrene and MMA

Scheme 3. Schematic Illustration for Photopolymerization of Perfluoro-2-methylene-4,5-dimethyl-1,3-dioxolane



could be synthesized via atom transfer radical polymerization. The block copolymerization was carried out in hexafluorobenzene using CBr_3-terminated poly(PMDD) (run 4 in Table 2) as a macroinitiator and MMA as a comonomer with CuCl/2,2′-bipyridine system at 100 °C. To the best of our knowledge, synthesizing block copolymers with perfluorinated and hydrogenated parts is still challenging, though the properties of this kind of block copolymer are quite interesting. The investigation on characterizing the copolymers is in progress. The ^{19}F NMR spectra of both polymers were recorded in hexafluorobenzene using chloroform-*d* as a locking solvent at 50 °C. The chemical shift was measured from $CFCl_3$ as an internal reference. The ^{19}F NMR spectrum of poly(PMDD) obtained under Ar atmosphere is shown in Figure 1A. In the spectrum, the signal centered at −80.5 ppm is assigned to the trifluoromethyl group ($-CF_3$). The signals between −102.0 and −118.0 ppm are assigned to the main-chain fluorines ($-CF_2-$). The signal centered at −124.3 ppm is assigned to the fluorines on the dioxolane ring (−OCF−).

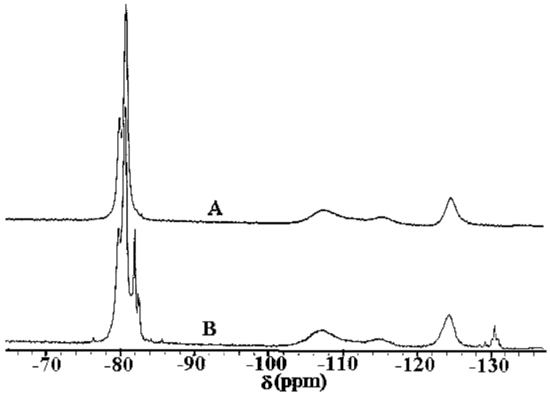


Figure 1. ^{19}F NMR spectra of poly(perfluoro-2-methylene-4,5-dimethyl-1,3-dioxolane)s obtained under Ar (run 3 in Table 1) (A) and under air atmosphere (run 5 in Table 1) (B).

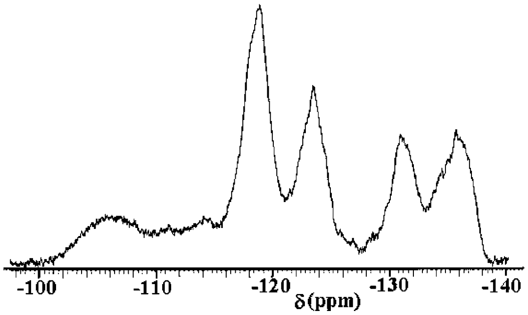


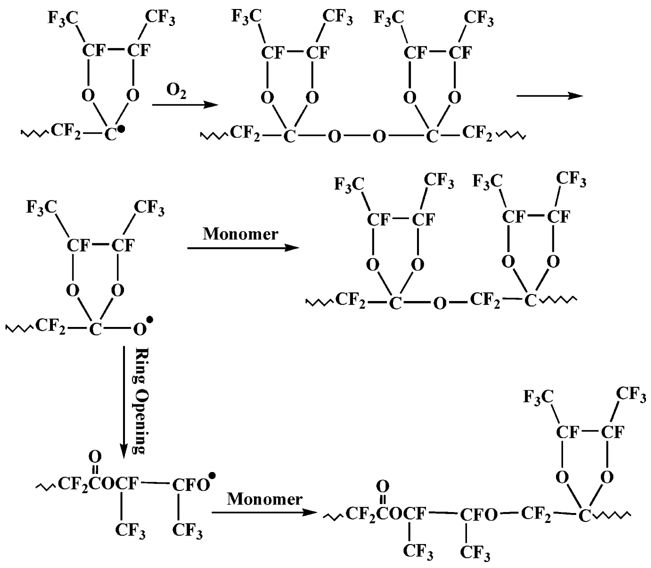
Figure 2. ^{19}F NMR spectrum of poly(perfluoro-3-methylene-2,4-dioxabicyclo[4.3.0]nonane) (run 2 in Table 1).

The ^{19}F NMR spectrum of poly(PMDN) obtained under an argon atmosphere is shown in Figure 2. In the spectrum, the four peaks centered at −118.8, −123.4, −130.8, and −135.6 ppm are assigned to the fluorines on the perfluorocyclohexane ring ($-CF_2-$ and −OCF−). The signals between −102.0 and −116.0 ppm are also assigned to the main-chain fluorines ($-CF_2-$) for poly(PMDN) according to the assignment for poly(PMDD). However, it overlaps with one of the side-chain peaks. It is noted that the area ratio of the signal between 102.0 and 127.6 ppm to the signal between 127.6 and 138.8 ppm is 2:1.

In addition, FTIR spectra of the obtained fluoropolymers were recorded to check the ring-opening possibility during radical polymerizations. Two very weak peaks ascribed to the carbonyl absorption of the end group of perfluorobenzoic ester at about 1795 cm^{-1} and the characteristic fluorinated benzene absorption at 1515 cm^{-1} are observed for the sample prepared in argon atmosphere. The results may suggest that ring opening did not occur during polymerizations. In other words, the percentage of the ring-opening part in the polymerizations of perfluorinated dioxolanes is undetectable using FTIR and NMR techniques. The hydrocarbon analogues of 2-methylene-1,3-dioxolanes were reported to produce a product containing ring-opening units via free-radical mechanism in most cases.[18] However, in the case of 3-methylene-2,4-dioxabicyclo[4.3.0]nonane, ring-opening did not occur during its radical polymerization.[18b] The fluorine in the monomers influences the ring-opening polymerization. Perfluorinated dioxolanes produced only vinyl addition polymers as we reported previously.[15] This was ascribed to that the fluorinated ether bond, $-O-CF_2-$, being quite strong and not cleaving during free-radical polymerization.

Oxygen Effect on the Polymerization. The radical polymerization under an air atmosphere was also performed. The conditions and results of polymerization are shown in Table 1. It was found that the presence of air did not affect the polymer yield. The polymerizations of PMDD at 60 °C in hexafluorobenzene produced 88% and 85% polymer in the presence of argon and air, respectively (runs 3 and 5 Table 1). The polymerizations of PMDN at 60 °C in hexafluorobenzene produced 46% and 35% polymers under argon and air atmosphere, respectively (runs 10 and 11 Table 1). This is interesting because the oxygen generally inhibits the free-radical polymerization of hydrocarbon vinyl monomers at 60 °C or lower temperature.[19] Oxygen reacts with radical species to form a relatively unreactive peroxy radical which reacts with itself or another propagating radical

Scheme 4. Oxygen Effect on the Radical Polymerization of Perfluoro-2-methylene-4,5-dimethyl-1,3-dioxolane



by coupling and disproportionation reactions to form peroxides and hydroperoxides. The formed peroxides and hydroperoxides are inactive at relatively low temperatures. The further initiation may occur at quite higher temperatures, resulting in the polymer containing an ether bond on the main chain.

In the case of fluorinated vinyl monomers, oxygen may also react with the radical species to form peroxides. However, the formed perfluorinated peroxide is not stable at 60 °C and readily produces new radical species to initiate the radical polymerization again. The perfluorinated peroxide has a lower decomposition temperature compared to its analogues. As a model comparison, *tert*-butyl peroxide (half-life $t_{1/2} = 10$ h at 126 °C) was used as a high-temperature radical initiator at about 110 °C, while perfluoro-*tert*-butyl peroxide was used as a radical initiator at 70 °C. Consequently, the polymerization under an air atmosphere may lead to a polymer containing an ether bond on the main chain. On the other hand, the ring opening may occur through breaking the C−O bond adjacent to the oxy radical to form a new radical which continues to initiate the polymerization, producing a product containing an ester part.

The structure of the polymer obtained in the presence of air was found to be different from that obtained under argon based on the ^{19}F NMR analysis. Compared with the ^{19}F NMR spectra of the sample obtained under argon and under air atmosphere (runs 3 and 5 in Table 1) (Figure 1), three new signals at about −81.9, −82.5, and −130.6 ppm appeared in the spectrum of the sample obtained under an air atmosphere. The fluorines on trifluoromethyl groups ($-CF_3$) and on the dioxolanes ($-OCF-$) may slightly shift to the higher field due to the dioxolane adjacency to the main chain $-OCF_2-$. The signals overlapped with the trifluoromethyl groups at about −82.5 ppm, which was ascribed to the fluorine on the main chain of $-OCF_2-$. The content of the new formed $-OCF-$ signal at −130.6 ppm is calculated to be about 21 mol % based on all $-OCF-$ signals. Considering ring opening from the adjacent C−O bond, the three new signals in the ^{19}F NMR spectrum could be also assigned as the $-CF_3$ (−81.9 ppm), $-OCF_2-$ (−82.5 ppm), and $-OCF-$ (−130.6 ppm) in the ester part. Thus, the oxygen effect may be schematically illustrated as shown in Scheme 4. The final product is a copolymer as shown in Scheme 4. The copolymer contains unstable units such as ester and/or ortho-acid ester. TGA proves the presence of unstable units. TGA of the product was performed under a nitrogen atmosphere using a heating rate of 10 °C/min. A clear two-step decomposition was observed as shown in Figure 3. The first step was ascribed to the unstable unit decomposition. It was found to be thermally unstable at about 133 °C. About 17% of the polymer was lost in this step between 133 and 300 °C. This is agreement with the calculated mole content of the ester and/or ortho-acid ester unit of about 21 mol % by fluorine NMR mentioned above. Thus, to obtain the thermally stable polymeric materials, it is necessary that the polymerization is performed under argon or nitrogen atmospheres and kept until the polymerization is totally completed.

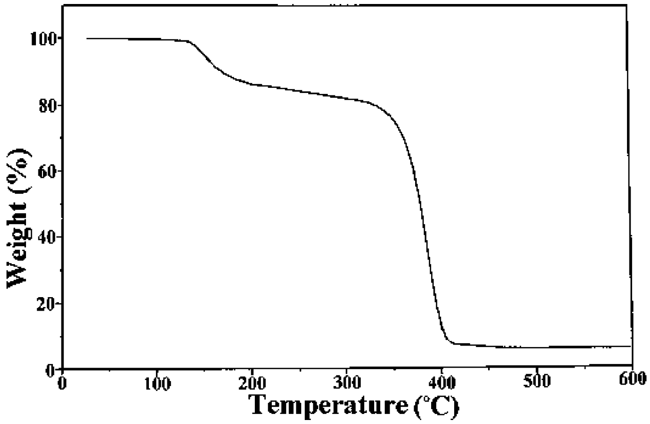


Figure 3. Thermogram of poly(perfluoro-2-methylene-4,5-dimethyl-1,3-dioxolane) obtained under air atmosphere (run 5 in Table 1).

On the other hand, it was reported that reaction of the perfluorinated double bond with oxygen is a general behavior of many fluoro olefins.[20] For example, the (photo)oxidation of tetrafluoroethylene and hexafluoropropylene with oxygen produced perfluoropolyethers.[20b] Perfluorodihydrodioxins slowly react with oxygen to form epoxides and acyl fluorides at 25 °C.[20c] That is why an acid gas was observed after storing the monomers for a long time under air. Therefore, storing those monomers should be under argon or nitrogen atmospheres at low temperature.

The reaction of fluorinated monomer with oxygen may also be responsible for the opacity of the polymer rod. We observed that a lower conversion of the monomer in the bulk polymerization led to a faster change in the opacity of the polymer rod and a deeper opacity upon it exposure to air. This may be ascribed to the fact that the unreacted monomer reacts with oxygen and moisture to form heterogeneous materials as mentioned above.

Kinetic Study on the Bulk Polymerization. The kinetic studies for the two monomers were performed in bulk at 50 °C at F-BPO concentration of 0.020 M. Time−conversion curves of the bulk homopolymerization are shown in Figure 4. The rate of polymerization (R_p) was calculated on the basis of the initial slope of the first-order plot for the monomer consumption rate. The rate of polymerization of PMDD was found to be 1.25×10^{-2} mol L^{-1} s^{-1}, whereas that of PMDN was found to be 5.0×10^{-3} mol L^{-1} s^{-1} at 50 °C. The rate of polymerization of PMDD is 2.5 times faster than that

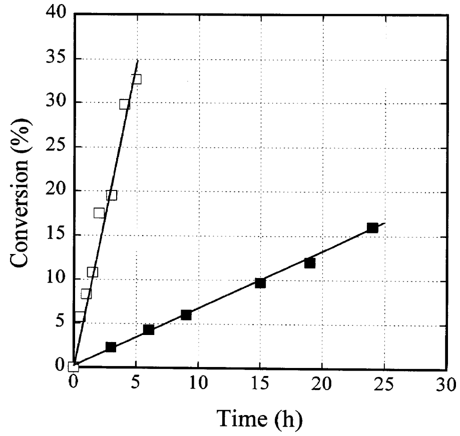


Figure 4. Time−conversion curves for the bulk polymerizations of PMDD (white squares) and perfluoro-3-methylene-2,4-dioxabicyclo[4.3.0]nonane (black squares) using perfluorobenzoyl peroxide as an initiator at 50 °C.

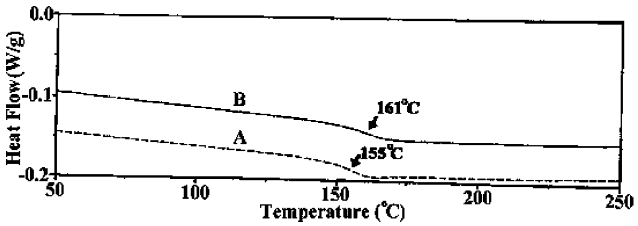


Figure 5. DSC curves for the poly(perfluoro-2-methylene-4,5-dimethyl-1,3-dioxolane) (run 3 in Table 1) (A) and poly(perfluoro-3-methylene-2,4-dioxabicyclo[4.3.0]nonane) (run 2 in Table 1) (B).

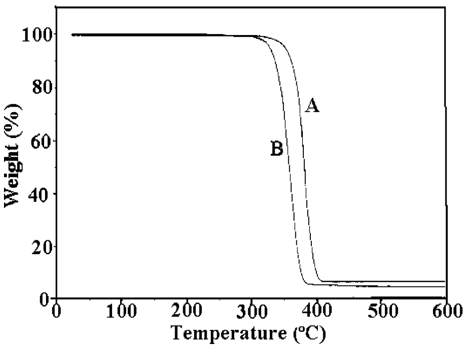


Figure 6. Thermograms of poly(perfluoro-2-methylene-4,5-dimethyl-1,3-dioxolane) (A) (run 3 in Table 1) and poly(perfluoro-3-methylene-2,4-dioxabicyclo[4.3.0]nonane) (B) (run 2 in Table 1).

of PMDN. This was ascribed to the steric effect in the polymerization of PMDN. The propagation is reasonably slow considering that a growing radical with steric hindrance attacks a monomer.

Physical Properties. The glass transition for poly(PMDD) and poly(PMDN) were determined by DSC at a heating rate of 10 °C/min. Both of them exhibited a clear glass transition as shown in Figure 5. Glass transition temperatures were found to be 155 and 161 °C for the poly(PMDD) and poly(PMDN), respectively.

TGAs of poly(PMDD) and poly(PMDN) were performed under a nitrogen atmosphere using a heating rate of 10 °C/min. The thermograms of poly(PMDD) and poly(PMDN) are shown in Figure 6. The onsets of decomposition for poly(PMDD) and poly(PMDN) are 368 and 342 °C, respectively. The lower thermal stability of the poly(PMDN) may be due to low molecular weight as observed by the intrinsic viscosity of this polymer. The low molecular weight polymer contains higher content of unstable end groups, which may cause an unzipped effect on the decomposition of the polymer.

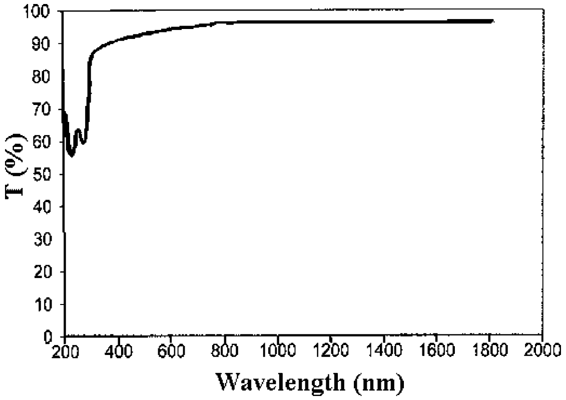


Figure 7. Transmission spectrum of poly(perfluoro-2-methylene-4,5-dimethyl-1,3-dioxolane) (thickness: 0.10 mm).

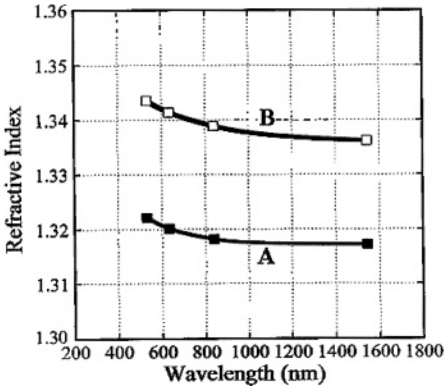


Figure 8. Refractive indices of poly(perfluoro-2-methylene-4,5-dimethyl-1,3-dioxolane) (A) and poly(perfluoro-3-methylene-2,4-dioxabicyclo[4.3.0]nonane) (B).

The free-standing film could be obtained from poly(PMDD) by casting. Poly(PMDN) cannot afford a free-standing film due to its brittleness. Hence, only the poly(PMDD) film was measured for the optical transmission. The vibration overtone of the stretching bond led to the absorption losses in POF. As Groh reported,[21] the carbon−fluorine (C−F) bond has a lowest absorption losses among carbon−hydrogen (C−H), carbon−deuterium (C−D), and C−F bonds in the near-IR region. As shown in Figure 7, the transmission spectrum of poly(PMDD) in the 200−2000 nm range illustrates the extraordinary optical transmission from the deep-UV to near-infrared regions for perfluoro-2-methylene-1,3-dioxolane polymers. This indicated that fluoropolymer could afford a low loss contribution in POF. On the other hand, water is observed to have a strong O−H absorption for the wavelengths over 700 nm. Generally, hydrogenated polymers have some water absorption. Fortunately, fluoropolymers typically have a comparatively low water absorption. Therefore, a fluoropolymer is an ideal material for POF.

The refractive indices of the films were measured at different wavelengths and shown in Figure 8. The refractive indices are dependent on the wavelength. The theoretical refractive indices were calculated to be 1.3361 and 1.3164 at the wavelength of 589 nm for poly(PMDN) and poly(PMDD), respectively, according to a reported method.[22] They are in good agreement with the experimental values reported here. The refractive indices for the fluoropolymers are low compared to those

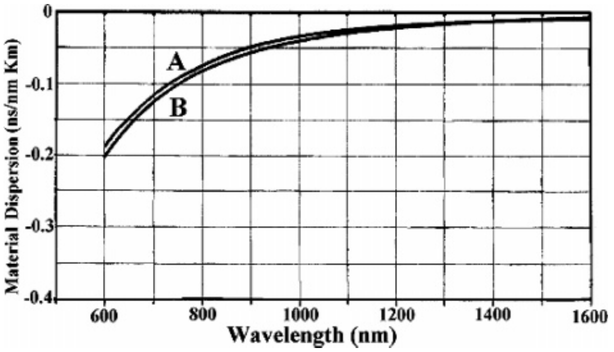


Figure 9. Material dispersions of poly(perfluoro-2-methylene-4,5-dimethyl-1,3-dioxolane) (A) and poly(perfluoro-3-methylene-2,4-dioxabicyclo[4.3.0]nonane) (B).

of the hydrocarbon polymers due to the presence of C−F bonds.

For plastic optical fiber communications, the bandwidth is strongly related to the material dispersion. The lower the material dispersion, the higher the bandwidth. The material dispersion could be calculated on the basis of the data in Figure 8 according to a reported method.[23] The results are shown in Figure 9 for both polymers between 600 and 1800 nm. The material dispersions of the two polymers are smaller than that of silica and PMMA and are basically the same as that reported for other fluoropolymers.[4b] This is one of the requirements in preparing the high bandwidth GI POF.

Conclusions

PMDD and PMDN are synthesized in a convenient way with high yield and low byproducts. Despite their strong steric hindrance, they could be polymerized in a simple way via the free radical mechanism.

Polymerizations of PMDD and PMDN in bulk and in hexafluorobenzene were carried out using perfluorobenzoyl peroxide as an initiator. The two monomers also allows the preparation of new fluoro- and perfluoro(co)-polymers.

Photopolymerizations of the two monomers in bulk and in hexafluorobenzene were also carried out in the presence of carbon tetrabromide or carbon tetrachloride under irradiation by UV light at about 365 nm. Photopolymerzation afforded polymers with a range of intrinsic viscosity from 3.6 to 13.3 mL/g. There are also available interesting fluorotelogens, -telomers, and/or -macromers with reactive end groups of $-CCl_3$ or $-CBr_3$.

The colorless and clear polymers with high glass transition temperature, low refractive index, low material dispersion, and extraordinary optical transmission from the deep-UV to near-IR regions have promising and interesting applications in the field of plastic optical fiber, pellicles, and antireflective coating materials.

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Note Added after ASAP Publication. This article was released ASAP on October 10, 2005. Table 1, Table 2, and paragraphs 6 and 8 in the Results and Discussion section have been revised. The correct version was posted on October 31, 2005.

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