Macromolecules **2005,** *38,* 4237−4245

Synthesis and Characterization of an Amorphous Perfluoropolymer: Poly(perfluoro-2-methylene-4-methyl-1,3-dioxolane)

František Mikeš,† Yu Yang,† Iwao Teraoka,† Takaaki Ishigure,‡ 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, 144-8 Ogura Saiwai-ku, Kawasaki 212-0054, Japan

Received January 14, 2005; Revised Manuscript Received March 23, 2005

ABSTRACT: A perfluorinated monomer, perfluoro-2-methylene-4-methyl-1,3-dioxolane (PFMMD), was synthesized by various methods. The monomer was polymerized in bulk and/or in the solution by a free radical mechanism using perfluorodibenzoyl peroxide and/or perfluorodi-*tert*-butyl peroxide as an initiators. The polymers obtained (poly(PFMMD)) were colorless and transparent. However, a polymer rod exposed to the atmosphere turned hazy. When the polymers were purified by precipitating the polymer solution into chloroform, they did not turn hazy when exposed to air for a long period of time and remained clear with a high UV−vis light transmittance. The glass transition temperature of the purified polymer was 130−134 °C. NMR measurements indicate that the purified polymers have mostly vinyl addition polymer structure. Nevertheless, we suppose that the pristine polymers contain structural units formed by ring-opening polymerization. The molecular weight of poly(PFMMD) samples can be regulated using carbon tetrachloride, carbon tetrabromide, and sulfuryl chloride as chain transfer agents. Polymerization in the presence of these regulators is characterized by nondegradative chain transfer. The intrinsic viscosity of poly(PFMMD) samples was determined in hexafluorobenzene. Hexafluorobenzene is a thermodynamically good solvent for poly(PFMMD). The molecular weights of poly(PFMMD)s were characterized by the intrinsic viscosity and dynamic light scattering (DLS). The refractive index of poly(PFMMD) between 400 and 1550 nm was between 1.3360 and 1.3270. The material dispersion of poly(PFMMD) is superior to that of a commercial poly(1,1,2,4,4,5,5,6,7,7-decafluoro-3-oxa-1,6-heptadiene) (Cytop).

Introduction

Recently, various plastic optical fiber (POF) materials have been increasingly applied in local area network (LAN) because elastic moduli of plastics are typically many times lower than those of silica. For this reason plastic fibers may have very large optical cores while maintaining acceptable minimum bend radii. Plastic fibers may be terminated simply by cutting without cleaning and polishing required by silica fibers. Consequently, the installed cost of a POF system is expected to be low due to easy installation and to relaxed tolerances of mechanical and optical couplings at end points.[1,2] As a result of these advantages, various POF materials have been recently developed. Poly(methyl methacrylate) (PMMA) along with other POF materials is commercially used in relatively short distance networking. PMMA has excellent transparency, is weatherproof, admits mass production, and is a low-cost polymer. However, the carbon−hydrogen bonds in PMMA absorb strongly in the near-infrared region of spectrum. When the hydrogen atoms in PMMA are replaced with heavier atoms such as deuterium or fluorine,[3−5] the optical absorption is decreased. Fluorine-substituted polyacrylates and polymethacrylates cannot be prepared. Thus, other types of perfluorinated amorphous polymers have been considered for POF materials. Asahi Glass Co., Japan, has successfully developed and commercialized the perfluorinated polymer poly(1,1,2,4,4,5,5,6,7,7-decafluoro-3-oxa-1,6-heptadiene) (Cytop).[6] Because this polymer is completely amorphous and contains no hydrogen, it shows excellent near-infrared transparency and exhibits negligible absorption losses at the most important telecommunication wavelengths. In searching for alternative perfluorinated amorphous polymers for optical applications, we came across another perfluoro amorphous polymer: poly(perfluoro-2-methylene-4-methyl-1,3-dioxolane) (poly(PFMMD)).[7]

The application of polymers as POF materials requires preparation of the polymers of desired properties such as reasonably high glass transition temperature (T_g), suitable molecular weight, flow temperature (T_f), mechanical strength, material dispersion [$M(\lambda)$], and attenuation. The calculated refractive index[8] for poly(PFMMD) and Cytop is 1.3214 and 1.3414, respectively. The T_g for poly(PFMMD) was reported higher than 110 °C. The lower refractive index of poly(PFMMD) and higher T_g in comparison with those of Cytop initiated our interest in poly(PFMMD). Information available on PFMMD and poly(PFMMD) is scarce. To the best of our knowledge, there is not a single report on basic molecular characterization of poly(PFMMD)s prepared under different reaction conditions. Therefore, we have investigated in detail the preparation of PFMMD and poly(PFMMD) and the physicochemical properties of the polymers obtained.

Experimental Part

Materials. Hexafluoropropylene oxide (**1**), hexafluorobenzene (HFB), chloropentafluorobenzene (CPFB), and Fluorinert FC-75(FC-75) were purchased from Syn.Quest, Inc. All other chemicals were obtained from Aldrich Chemical Co. Bis(2-ethoxyethyl) ether was stirred with CaH_2 and vacuum-distilled from CaH_2, all other chemicals were used as received.

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† Polytechnic University.
‡ Keio University.

10.1021/ma050085u CCC: $30.25

Methyl 3,3,3-trifluoropyruvate (**7**) was prepared[9] starting from **1** via methyl 2,3,3,3-tetrafluoro-2-methoxypropanoate, which was transformed to **7** using sulfuric acid. 2-Trifluoromethyl-2,4,4,5,5-pentachloro-1,3-dioxolane (TFCD) was prepared by chlorination[10] of 2-carboxymethyl-2-trifluoromethyl-1,3-dioxolane in the presence of ultraviolet radiation in CCl_4 at temperature below 80 °C. Perfluorodibenzoyl peroxide (PFDBP) was prepared by reaction of pentafluorobenzoyl chloride with hydrogen peroxide.[11] Half-life at 68 °C was 10 h.[12] The crude initiator was recrystallized from petroleum ether (bp 40−60 °C); mp 76−78 °C (lit.[11] mp 76−78 °C). Perfluorodi-*tert*-butyl peroxide was prepared by reaction of perfluoro-*tert*-butyl acohol with chlorine trifluoride.[13] Pure peroxide was obtained by vacuum fractionation and identified by ^{19}F NMR and mass spectrometry.

Characterization. ^{1}H, ^{19}F, and ^{13}C NMR spectra were taken using a Bruker ACF 300 spectrometer (300 MHz for ^{1}H, 75 MHz for ^{13}C measurement). ^{19}F NMR spectra were observed at frequency 282 MHz with fluorotrichloromethane as standard. A 5 mm NMR tube with an insert filled with $CDCl_3$ or DMSO-d_6 was used as an internal lock.

FTIR spectra were obtained with a Perkin-Elmer FTIR-1600 spectrometer.

GC-MS analyses were performed using an HP 5890 gas chromatograph and an HP 590 B mass spectrograph. A J&W GC capillary column (30 m × 0.25 mm × 1.4 μm film) with stationary phase DB-624 was used for analysis (helium carrier gas).

Differential Scanning Calorimetry (DSC). A DSC 2920 module with the TA Instrument 5100 system was used for measurements. Samples weighing 7−15 mg were measured. The glass transition temperature (T_g) (10 K/min) was determined as an endothermic shift in the second heating scan.

Thermal Gravimetric Analysis (TGA). The analysis of the polymers and salts of perfluoro-2,4-dimethyl-1,3-dioxolane-2-carboxylic acid (**6**) was performed using aforementioned equipment with TGA module (10 K/min).

Viscometry. Viscosities of a solvent and filtered polymer solutions were measured using a modified Ubbelohde viscometer at 25 ± 0.05 °C in a thermostat bath. The intrinsic viscosity was evaluated using the Huggins equation.

Dynamic light scattering (DLS) measurements were performed using a particle-sizing system (Beckman-Coulter, N4 Plus). The light source was a He−Ne laser at wavelength λ = 632.8 nm. Solutions of polymers in HFB were filtered through PTFE 0.45 μm and/or 0.20 μm filters (DISMIC, Advantec, Tokyo Roshi Kaisha, Ltd, Japan). Measurements were performed at scattering angles 10.7°, 15.2°, 22.2°, 29.1°, 63.5°, and 90° at 25 °C. Because of the low d*n*/d*C* of poly(PFMMD) in HFB, analysis of autocorrelation functions of light scattering intensity using CONTIN[14] was unreliable. For this reason three series of the autocorrelation functions (each 12−20 runs) were acquired for each sample, concentration, and angle. For polymer no. 84 having the lowest molecular weight and at the lowest concentration, data were accumulated for 600, 900, 1200, 2400, 3000, and 3600 s at angles 10.7°, 15.2°, 22.2°, 29.1°, 63.5°, and 90°, respectively. The runs with a baseline error greater than 0.05% for angles 29.1°, 63.5°, and 90° and 0.5% for angles 10.7°, 15.2°, and 22.2° were discarded. The remaining runs were averaged and analyzed. The intensity autocorrelation function $g_2(\tau)$ at delay time τ for homodyne detection was analyzed by the cumulant method[15]

$$g_2(\tau) = \exp\left[2\left(C_0 - \langle\Gamma\rangle\tau + \frac{\mu_2\tau^2}{2}\right)\right] + g_2(\infty) \tag{1}$$

where $g_2(\infty)$ is the baseline and $\langle\Gamma\rangle$ and μ_2 are the first and second cumulants of the decay rate Γ in the autocorrelation function of the electric field. $\langle\Gamma\rangle$ is related to the mutual diffusion coefficient D_m as

$$\langle\Gamma\rangle = D_m k^2 \tag{2}$$

where k is the scattering wave vector. At scattering angle θ, $k = (4\pi n/\lambda)\sin(\theta/2)$, where n is the refractive index of the solvent. Usually, the variance μ_2 is appropriately normalized as polydispersity $\equiv 4\mu_2/\langle\Gamma\rangle^2$. The cumulant method is applicable for distributions of Γ which are not broad ($\mu_2/\langle\Gamma\rangle^2 \le 0.4$). The molecular weight distribution index can be estimated $M_z/M_w \cong 1 + 4\mu_2/\langle\Gamma\rangle^2$.

The value of D_m was evaluated in the plot of $\langle\Gamma\rangle$ vs k^2 at each concentration. Then, D_m was plotted as a function of polymer concentration C to obtain the single-chain diffusion value D_0, which is defined by

$$D_m = D_0(1 + k_D C + ...) \tag{3}$$

with a linear coefficient[16] k_D given by

$$k_D = 2A_2M - \xi_1 - \gamma_{sp} \tag{4}$$

where $2A_2M_w$ represents the thermodynamic interaction term, ξ_1 represents the hydrodynamic interaction term, and the γ_{sp} term corrects for the solvent backflow. Because of a low d*n*/d*C* of poly(PFMMD) and chemical resistivity problems of many wet parts used in liquid chromatography when the mobil phase is a fluorinated solvent, it is difficult to characterize the polymers in size exclusion chromatography. Characterization using DLS is then an acceptable alternative.

The specific refractive index increment (d*n*/d*C*) value of the polymer solution in HFB and binary solvent HFB/CPFB (60/40 v/v) was determined using a Bruice-Phoenix differential refractometer (model Bp-2000-V) at 25 °C for a wavelength of 546 nm.

Refractive index measurement of bulk polymer samples and films was carried out using a prism coupler[17] (Metricon, modul 2010). The refractive indices were measured with accuracy of ±0.0005. The probe wavelengths in the prism coupler were 409, 450, 521, 633, 650, 780, 834, 1000, 1101, 1300, and 1546 nm. Coupling profiles as a function of incident angle were analyzed with the 2010 system software.

The refractive index data as a function of wavelength were fit to a three-term Sellmeier equation to calculate $d^2n/d\lambda^2$ in eq 5.

The material dispersion coefficient $[M(\lambda)]$ represents broadening of a pulse per unit length of optical fiber and unit spectral width and is given by

$$M(\lambda) = -\frac{\lambda}{c}\frac{d^2n}{d\lambda^2} \tag{5}$$

where c is the velocity of light in vacuo.

Monomer Preparation. The synthetic routes are shown in Schemes 1, 2, and 3.

The intermediates for preparation of monomer PFMMD were prepared according to a Du Pont patent[7] (Scheme 1).

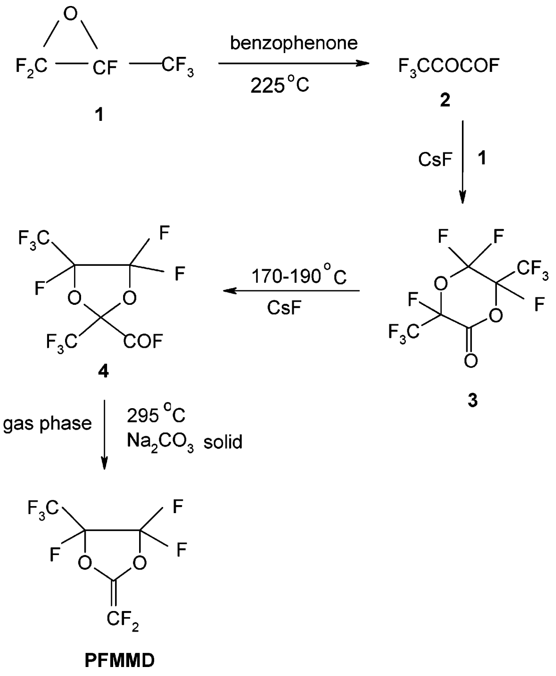
The structure of intermediate perfluoro-2-oxo-3,6-dimethyl-1,4-dioxane (**3**) was confirmed by ^{19}F NMR (δ ppm, $CDCl_3$): −113.3, −117.0 (1 F, $OC\boldsymbol{F}(CF_3)C{=}O$); −82.6 (3F, $OCF(C\boldsymbol{F_3})C{=}O$); −81.0, −94.0 (2F, CF_2); −126.0, 128.0 (1F, $OC\boldsymbol{F}(CF_3)CF_2$); −81.1 (3F, $OCF(C\boldsymbol{F_3})CF_2$). Perfluoro-2,4-dimethyl-2-fluorocarbonyl-1,3-dioxolane (**4**) was isolated from the reaction mixture by a fractional distillation. Fluorocarbonyl **4** was obtained in 69% yield; bp 60−60.5 °C. ^{19}F NMR (δ ppm, $CDCl_3$): −124.5, −126.0 (1F, $CF_3C\boldsymbol{F}$), −81.1 (3F, $\boldsymbol{F_3}C$ CF), −81.0, −84.0 (2F, CF_2); −81.7 (3F, $\boldsymbol{F_3}CCCOF$); +23.5, +24.3 (1F, COF).

Decarboxylation of **4** was carried out in the gas phase. PFMMD was obtained in very low yield.

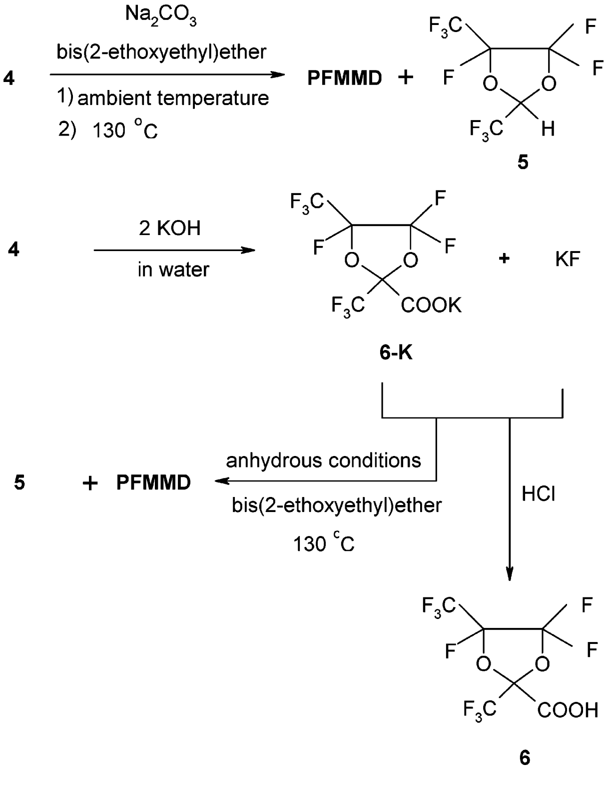
Decarboxylation of fluorocarbonyl **4** was carried out also in anhydrous bis(2-ethoxyethyl) ether[18] (Scheme 2). A decomposition product was analyzed by GC-MS and ^{19}F NMR. It was found that it consists of a mixture of **4**, PFMMD, and perfluoro-2-hydro-2,4-dimethyl-1,3-dioxolane (**5**).

Decarboxylation of **6**-K in a mixture with the byproduct potassium fluoride was also carried out in thoroughly dried bis(2-ethoxyethyl) ether (Scheme 2). The aforementioned mixture was prepared by reaction of **4** with 2 equiv of potassium hydroxide in aqueous solution. Most of the water

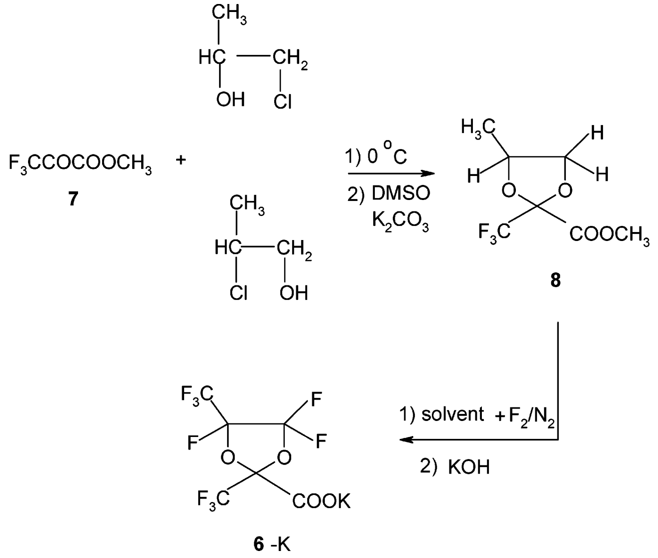
Scheme 1. Synthetic Route to PFMMD[7]



Scheme 2. Decarboxylation of Fluorocarbonyl 4, Potassium Salt 6-K, in Bis(2-ethoxyethyl) Ether and Preparation of 6



Scheme 3. Synthesis of Potassium Salt 6-K from Methyl 3,3,3-Trifluoropyruvate by Direct Fluorination



was evaporated, and the residue was dried at 90−120 °C under vacuo at 10^{-1} Torr. Decarboxylation was carried out in a three-necked round-bottomed flask equipped with a gastight mechanical stirrer, thermometer, and short path head. The flask was charged with 255 g of bis(2-ethoxyethyl) ether and 165 g of equimolar mixture of **6**-K with potassium fluoride. The reaction mixture was heated at 130 °C under stirring. Products of the decarboxylation reaction were condensed in a trap placed in an ethanol−dry ice mixture and then distilled. The distillate (bp 40−55 °C) was washed at least three times with ice-cold aqueous solution sodium hydroxide (3 wt %) and water and dried over anhydrous magnesium sulfate. According to GC-MS analysis, the crude product consisted of PFMMD and **5**. The mixture was fractionally distilled using a spinning band distillation system. Nevertheless, we could not successfully separate PFMMD and **5**.

Pure **5** was prepared by decarboxylation of **6**-K in a mixture of ethylene glycol with bis(2-ethoxyethyl) ether (1/1 by weight). **6**-K (142 g) and an ethylene glycol/diethylene glycol mixture (200 g) were heated under a reflux condenser, which was connected to two condensing traps. The reaction began when the flask content reached 130 °C. Over a period of 3 h, the temperature was raised to 210 °C. The crude product was washed four times with ice-cold 5 wt % aqueous solution of sodium hydroxide and with water. The crude product was dried with ($MgSO_4$) and fractionated; yield 67 g (62%); bp 50.8 °C. **5** GC/MS: m/e ($M^{\bullet+} - 1$) 263 (0.3%), ($M^{\bullet+} - 69$) 195 (26%), 147 (18%), 119 (25%), 97 (29%), 69 (100%), 51 (36). ^{1}H NMR (δ ppm, $CDCl_3$): 5.88; 5.77 (CH).

Perfluoro-2,4-dimethyl-1,3-dioxolane-2-carboxylic acid (**6**) was prepared from its potassium salt in mixture with equimolar amount of potassium fluoride. **4** (147 g, 0.474 mol) was added dropwise into an aqueous solution (600 mL) of potassium hydroxide (0.948 mol). Water was then vacuum-evaporated to one-third of the original volume, and concentrated hydrochloric acid (250 mL) was added. The bottom layer was separated and fractionally distilled under reduced pressure. 142 g of the acid **6** was obtained (yield 93%); bp 103−104 °C/100 Torr. ^{1}H NMR (δ ppm, D_2O): 4.63, 4.64 (COOH), (δ ppm, DMSO-d_6) 6.60 (COOH). ^{19}F NMR: −78.4 m, −78.9 m, −79.2 m, −79.7 m, −84.1 d, −84.3 d, −84.6 d, −84.8 d (2F, CF_2); −80.8 d, −81.2 d, −81.8 m (6F, $C\boldsymbol{F_3}CF$ and$C\boldsymbol{F}_3CCOOH$), −124.8 m, −125.0 m (1F, CF). The purity of the acid was confirmed by acid−base potentiometric titration. The weight per equivalent was 310.23 g (formula weight of the acid is 308.07 g/mol).

Potassium, sodium, and cesium salts of **6** were prepared by neutralization of an aqueous solution of acid with the equimolar quantity of the standardized solutions of particular hydroxides. The initial decomposition temperatures for sodium, potassium, and cesium salts were 300, 258, and 201 °C, respectively.

Liquid-phase fluorination of 2-carboxymethyl-2-trifluoromethyl-4-methyl-1,3-dioxolane (**8**) was carried out in collaboration with Exfluor Research Co., Texas.

8 was prepared (Scheme 3) analogously to preparation of 2-carboxymethyl-2-trifluoromethyl-1,3-dioxolane.[10] Crude product was fractionally distilled (bp 77−78 °C/12 Torr; yield 77%). ^{1}H NMR (δ ppm, $CDCl_3$): 4.2−4.6, 3.6−3.8 (m, 3H, $CHCH_2$), 3.85−3.88 (m, 3H, $COOCH_3$), 1.36−1.43 (m, 3H, CCH_3). ^{19}F NMR (δ, ppm): −81.3 (s, 3F, CF_3).

Fluorination of **8** (290 g) in a fluorinated solvent was performed using fluorine diluted with nitrogen. Solvent and byproducts were distilled off after fluorination, and the product was neutralized with aqueous potassium hydroxide. After water was partially evaporated in vacuo, an excess of concentrated hydrochloric acid (500 mL) was added. The bottom layer was separated and fractionally distilled under reduced pressure. The fraction bp 103−106°C/100 Torr was the acid **6** obtained in 64.8% yield. The boiling point and ^{19}F NMR spectrum of the acid were exactly the same as of acid previously prepared starting from **4** (Scheme 2).

Pure PFMMD was finally prepared by decomposition of **6**-K in solid state. An equimolar mixture of salt **6**-K and potassium fluoride (overall amount 204.3 g) was charged in a two-necked round-bottomed flask equipped with short path head and argon inlet. Decarboxylation was carried out at 260−290 °C. The rate of decarboxylation can be controlled by temperature. The decomposition products were collected in two consecutive traps (dry ice−ethanol) (crude product 110.7 g) and simple distilled. The distillate was washed with an ice-cold aqueous solution of 3 wt % sodium hydroxide and water and dried using anhydrous magnesium sulfate. The crude monomer (54.8 g, 44.4%) was fractionally distilled. Fractions were analyzed by GC-MS. 50.7 g of pure PFMMD was obtained (41.1% of theoretical yield); bp 44 °C. ^{19}F NMR (δ ppm, CDCl$_3$): −129.7 (1F, CF); −125.8, −126.3, −127.2, −127.7 (2F, =CF$_2$); −82.9, −83.5, −89.0, −89.5 (2F, CF$_2$); −81.2 (3F, CF$_3$). GC/MS: *m/e* (M$^{\bullet+}$) 244 (13%), 225 (3%), 197 (2%), 175 (1%), 150 (15%), 131 (25%), 100 (51%), 78 (100%), 50 (85%).

Polymerization. Polymerization of PFMMD was carried out in most cases in glass ampules (i.d. 0.8 cm). The monomer containing a desired amount of the initiator and eventually a chain transfer agent was filtered using a 0.45 μm Puradisc 25TF (Whatman). Glass ampules were charged with polymerization mixture and sealed after repeating of three times cycle freeze−pump−thaw. Polymerizations were carried out at 60 ± 0.1 °C. For samples containing the chain transfer agent conversion was kept below 17%. The polymers obtained were dissolved in HFB, the solutions were filtered, and polymers were recovered by precipitation in chloroform and dried in vacuo.

Polymerization experiments performed to determine the reaction order with respect to PFMMD were done in the mixture with **5** at 48 °C in similar manner as aforementioned experiments. Conversion was kept as low as possible (10−15%) and was determined gravimetrically after certain polymerization time. The polymerization rate $[-(M - M_0)/\Delta t]$ was evaluated from the linear part of the dependence of monomer concentration vs reaction time within the conversion range 0−10%.

The densities of PFMMD and of three different mixtures of the PFMMD with **5** were determined with a 10 mL pycnometer of the Guy-Lussac type with cap. The densities were within experimental error the same and equal to 1.61 g/mL at 20 °C.

Results and Discussion

Monomer Synthesis. Monomer PFMMD was prepared by various methods. It was initially prepared according to a Du Pont patent.[7] The monomer was reported being prepared starting from hexafluoropropylene oxide (**1**) via perfluoropyruvyl fluoride (**2**), perfluoro-2-oxo-3,6-dimethyl-1,4-dioxane (**3**), and perfluoro-2,4-dimethyl-2-fluorocarbonyl-1,3-dioxolane (**4**), as shown in Scheme 1. **2** was prepared with lower yield than has been reported,[7] and rearrangement of **3** proceeds with reasonable rate at temperature higher than 170 °C (ref 7, 150 °C). Decarboxylation of **4** was carried out in the gas phase in a column with loosely packed bed of anhydrous sodium carbonate at 295 °C in a current of argon as was described in the patent.[7] However, we obtained only a small amount of the monomer (~5%). Most of the starting fluorocarbonyl **4** carbonized at the beginning of the column. At lower temperature (e.g., 100−150 °C) no reaction took place, and the majority of the starting fluorocarbonyl **4** was recovered.

Decarboxylation of fluorocarbonyl **4** was reported to proceed in purified bis(2-ethoxyethyl) ether containing anhydrous sodium carbonate[18] (Scheme 2). Fluorocarbonyl **4** was added at ambient temperature in a suspension of anhydrous sodium carbonate in anhydrous bis(2-ethoxyethyl) ether, and the reaction mixture was then heated at 130 °C with stirring. The product of the decarboxylation reaction consisted of starting material, a small quantity of PFMMD and of saturated compound **5**. This method did not afford the monomer PFMMD in 55% yield as has been reported.[18] Most of fluorocarbonyl **4** carbonized in the reaction mixture. Bis(2-ethoxyethyl) ether was replaced by perfluoro(tetradecahydrophenanthrene). In this case no reaction took place, and the starting material was recovered.

Decarboxylation of dry **6**-K in the mixture with the byproduct potassium fluoride in anhydrous bis(2-ethoxyethyl) ether produced PFMMD and **5** which could not be separated using even an efficient spinning band distillation column. The starting mixture contained PFMMD and **5** in the ratio approximately 1:1. The hydrogen in **5** may be abstracted from solvent.

Pure **5** was prepared by decarboxylation of **6**-K in a mixture of ethylene glycol and bis(2-ethoxyethyl) ether (50:50 wt %).

Finally, PFMMD was obtained by decarboxylation in the solid state. Decarboxylation of dry **6**-K in the mixture with potassium fluoride was carried out at 260−290 °C. The rate of decarboxylation can be controlled by temperature. The decomposition products were collected and simple distilled, distillate was washed with an ice-cold aqueous NaOH solution (3 wt %) and dried over anhydrous magnesium sulfate, and pure PFMMD was obtained by fractional distillation (yield ~ 42%).

Direct fluorination of hydrocarbon esters has been reported to afford perfluorinated acids in a high yield;[19] the dioxolane derivatives bearing a fluorinated ester group have also been reported to be fluorinated in a good yield.[20] Thus, we have synthesized **6**-K by direct fluorination of **8,** as described in Scheme 3. The overall yield of the acid **6** was 65% (based on **8**).

Polymer Preparation. In the polymerization of PFMMD initiated by perfluorodibenzoyl peroxide, the reaction order with respect to initiator is 0.47, a slightly lower than 0.50 given by classical theory.[21] The lower reaction order may be due to the cage effect. On the basis of performed experiments, one cannot unequivocally decide which effect is operating. The reaction order with respect to PFMMD for polymerization in **5** is 1.18. A reaction order with respect to monomer different from 1.0 has been observed for a number of systems and has been interpreted in various manners.[22]

Polymerizations of PFMMD were carried out in bulk and/or in the solution. Polymerizations in bulk were carried out at 60 °C for 24 h, and in order to obtain high conversion, the polymerization temperature was gradually increased to 110 °C. The polymers isolated were dissolved in HFB and then precipitated in chloroform and dried in vacuo.

Poly(PFMMD)s prepared in bulk were colorless and transparent. However, when polymer samples in form of rod were exposed for 2 or 3 weeks to atmosphere at room temperature, they turned hazy and surface be-

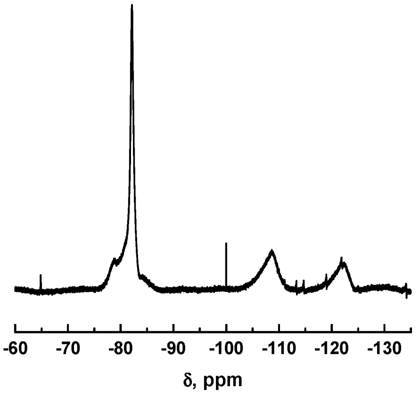


Figure 1. ^{19}NMR spectrum of purified poly(PFMMD)-63.

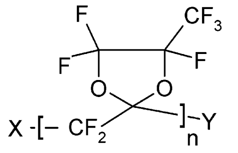


Figure 2. Chemical structure of poly(PFMMD).

came acidic. When pristine samples were heated to 260−290 °C, they colored to yellowish-brown and in molten samples formed bubbles. The purified and dried polymers were clear and did not color even when they were exposed to air for a long period of time. We surmise that the haze can be caused by hydrolysis of labile perfluoroester structural units formed by ring-opening polymerization. The T_g of the pristine high molecular weight polymers was ∼117 °C, but T_g of the purified polymers increased to 131−134 °C.

Polymerization of PFMMD in bulk was also initiated by perfluorodi-*tert*-butyl peroxide. The high molecular weight pristine and purified poly(PFMMD)s have T_gs of ∼116−117 and ∼134−135 °C, respectively.

The purified poly(PFMMD)s have good thermal stability, and the initial decomposition temperatures (under N_2 atmosphere) are higher than 370 °C.

The ^{19}F NMR spectra of the purified poly(PFMMD)s indicate that the vinylidene fluorines (−125.8, −126.3, −127.2, −127.7 ppm) observed in the monomer are not present. The signal at −108.8 ppm was assigned to fluorine atoms of the $-CF_2-$ group in the polyacetal main chain. The overlapping signals at −79.9 and −81.9 ppm were assigned to $-CF_2-$ and $-CF_3$ fluorine atoms of dioxolane ring, respectively. The signal at −122.8 ppm was assigned to $-CF-$ fluorine of the perfluorinated dioxolane ring (Figure 1). ^{19}F and ^{13}C NMR measurements indicated that the feasible ring-opening structural units formed in bulk polymerization were removed by hydrolysis. Purified polymers have structure as polymers prepared by vinyl addition (Figure 2).

The intrinsic viscosity [η], the glass transition temperature (T_g), and Huggins coefficient (k') of purified poly(PFMMD)s prepared in bulk are summarized in Table 1. Those of the polymers prepared in solutions of **5** and/or HFB are listed in Table 2. The intrinsic viscosity decreases with an increasing initiator concentration, as expected. The upper part of Figure 3 shows a plot of T_g of the polymers as a function of [η] for samples prepared in bulk and solutions with different initiator concentrations. In both polymerization environments, T_g increases with increasing [η]. It appears that T_g does not approach a plateau, in contrast to the prediction of the free volume theory. The T_g is higher and the increase in T_g is smaller for the polymers prepared in solutions compared with those of the polymers prepared in bulk. The difference might be ascribed to a broader distribution of the molecular weights of the polymers prepared in bulk that have a higher conversion of monomer than the polymers prepared in solution.

The lower part of Figure 3 shows that for polymers prepared in solutions the Huggins coefficient (k') decreases linearly with an increasing [η], whereas for polymers prepared in bulk the decrease in k' slows down. There is no consensus in the literature concerning the influence of the molecular weight distribution on the Huggins coefficient.

The molecular weight of poly(PFMMD)s was controlled by deliberate addition of carbon tetrachloride, carbon tetrabromide, surfuryl chloride, and/or 2-trifluoromethyl-2,4,4,5,5-pentachloro-1,3-dioxolane (TFED) to the reaction mixture. Table 3 lists T_g, [η], and k' for the polymer samples thus prepared. For reference, data are also listed for polymer samples prepared in the absence of the transfer agent. As seen in the change of T_g and [η], the most efficient chain transfer agents are surfuryl chloride and carbon tetrabromide. From the kinetic data of the PFMMD polymerization in bulk in the absence and presence of the chain transfer agents, one can conclude that polymerization is characterized by nondegradative chain transfer.

Light Scattering Measurement. The determination of molecular parameters using laser light scattering (LLS) of partially and fully fluorinated polymers was pioneered by Chu and co-workers.[23−26]

The light scattering intensity of a polymer solution is proportional to $(dn/dC)^2$. It is known that a perfluorinated polymer and a perfluorinated solvent are nearly isorefractive. Accurate determination of dn/dC for poly(PFMMD) in a perfluorinated solvent is important to achieve the desired precision in the static laser light scattering results, although it is difficult. Poly(PFMMD) is soluble at ambient temperature in HFB, Fluorinert FC-75 solvent, and in binary mixtures of HFB and CPFB containing more than 50 wt % of the first component. At 65 °C, poly(PFMMD) is soluble also in CPFB. The refractive index was measured for solutions of poly(PFMMD) (sample no. 85) in HFB and HFB/CPFB (60/40 w/w) at 546 nm, 25 °C at several concentrations up to ∼0.10 g/mL. A linear fitting gives $dn/dC = -0.0109 \pm 0.0002$ and -0.0175 ± 0.0004 mL/g for the two solvents, respectively. Such dn/dC values are too small to conduct characterization of polymer by static light scattering. In fact, static light scattering measurements using the modified photogoniodifusimeter Sofica (equipped with a 8 mW He−Ne laser) were attempted but not successful. The binary mixture has a greater dn/dC, but its absolute value is less than twice as large as that of HFB solutions. Furthermore, comparison of the intrinsic viscosity of the same polymer in HFB ([η] = 0.64 dL/g, 25 °C) and in HFB/CPFB (60/40 w/w) ([η] = 0.37 dL/g, 25 °C) indicates that the binary solvent is thermodynamically inferior to HFB. The light scattering measurements may be further complicated by preferential sorption of HFB from the binary solvent on the polymer coils. Therefore, we did not attempt light scattering measurements of the polymer solutions in the binary solvent.

Dynamic Light Scattering. Although the scattering intensity was weak and the decaying component was

Table 1. Properties of Poly(perfluoro-2-methylene-4-methyl-1,3-dioxolane)s Prepared in Bulk[a]

sample no.	initiator (wt %)	T_g (°C)	[η] (dL/g)	k'	$D_0 \times 10^{11}$ (m^2/s)	$k_D \times 10^3$ (L/g)	R_H (nm)	$M \times 10^{-6}$ (g/mol)
56	0.135	134.4	0.61	0.63	0.769	12.3	51	3.1
57	0.297	132.5	0.52	0.57				
58	0.491	131.8	0.45	0.65				
59	0.796	132.1	0.43	0.64	0.969	7.8	40	2.0
62	3.03	130.6	0.23	0.70				
63	4.56	131.2	0.20	0.80	1.267	1.3	31	1.25

[a] Polymerization temperature 60 °C, polymerization time 24 h, yield of polymers was in range 75−90%; intrinsic viscosity - HFB, 25 °C; initiator - perfluorodibenzoyl peroxide.

Table 2. Properties of Poly(perfluoro-2-methylene-4-methyl-1,3-dioxolane)s Prepared in Solution of Perfluoro-2-hydro-2,4-dimethyl-1,3-dioxolane and/or Hexafluorobenzene[a]

sample no.	initiator (wt %)	T_g (°C)	[η] (dL/g)	k'	$D_0 \times 10^{11}$ (m^2/s)	$k_D \times 10^2$ (L/g)	R_H (nm)	$M \times 10^{-6}$ (g/mol)
Perfluoro-2-hydro-2,4-dimethyl-1,3-dioxolane								
85	0.102	135.6	0.64	0.36	0.863	1.01	44	2.4
67	0.112	134.6	0.45	0.63				
68	0.397	134.3	0.31	0.80	0.950	1.38	41	2.1
86	1.734	132.9	0.15	0.97	1.501	0.767	26	0.9
Hexafluorobenzene								
92	0.098	133.7	0.30	0.70				
93	0.44	134.5	0.20	0.72				
94	1.66	133.5	0.15	0.73				

[a] Monomer/solvent mixture 38/62 (w/w), polymerization temperature 60 °C, polymerization time 24 h, yield of polymers was in range 50−80%; intrinsic viscosity - HFB, 25 °C; initiator - perfluorodibenzoyl peroxide.

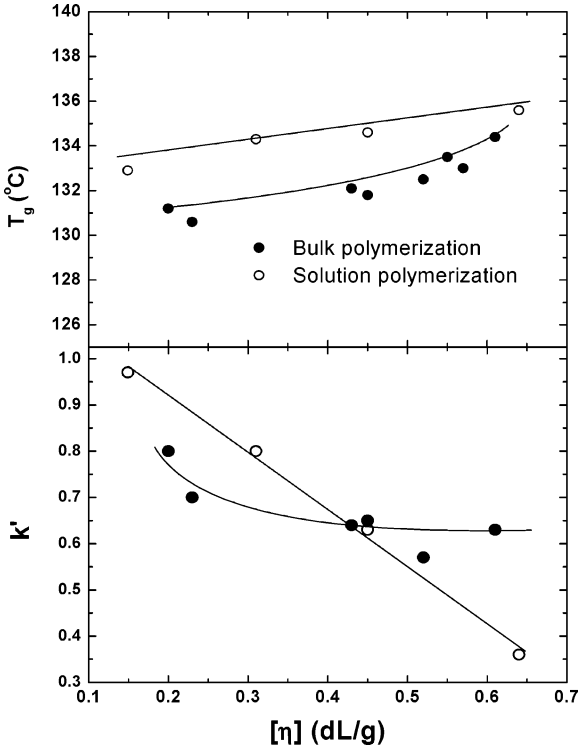


Figure 3. Dependence of the glass transition temperature (T_g) and of the Huggins coefficient (k') on the intrinsic viscosity ([η]) for poly(PFMMD)s prepared by polymerization in bulk and in solution with 2-hydro-2,4-dimethyl-1,3-dioxolane.

Table 3. Polymerization of Perfluoro-2-methylene-4-methyl-1,3-dioxolane in the Presence of Chain Transfer Agents

sample no.	initiator (wt %)	transfer agent (wt %)	T_g (°C)	[η] (dL/g)	k'	$M \times 10^{-5}$ (g/mol)
Carbon Tetrachloride						
64	0.50	0	133.6	0.45	0.65	15.0
65	0.50	0.36	132.2	0.36	1.01	
66	0.50	1.02	131.2	0.32	0.83	
Carbon Tetrabromide						
76	0.538	0	133.0	0.57	0.31	
77	0.538	0.52	124.7	0.048	5.77	
78	0.538	1.13	119.7	0.039	1.57	1.7
79	0.538	2.74	100.4	*a*		
Carbon Tetrabromide						
81	0.579	0	133.2	0.54	0.70	
82	0.579	0.129	130.1	0.12	1.29	
83	0.579	0.237	128.1	0.093	1.03	2.6
84	0.579	0.341	126.8	0.074	1.40	2.5
Surfuryl Chloride						
69	0.489	0	133.5	0.55	0.45	
70	0.489	1.30	113.9	*a*		
71	0.489	2.54	99.2	*a*		
2-Trifluoromethyl-2,4,4,5,5-pentachloro-1,3-dioxolane (TFCD)						
72	0.460	0	133.6	0.50	0.67	
73	0.460	1.26	133.8	0.50	0.55	
74	0.460	2.87	133.3	0.47	0.60	

[a] Very low [η]; polymerization temperature 60 °C; conversion of monomer less than 17%; intrinsic viscosity - HFB, 25 °C; initiator - perfluorodibenzoyl peroxide.

only a small part of the intensity autocorrelation function, we could successfully characterize the polymers using DLS. Figure 4 shows the scattering intensity autocorrelation functions $g_2(\tau)$ at all of six scattering angles and for a 25.35 g/L solution of poly(PFMMD)-56. The data are noisy at 90° only; the excess intensity of scattered light is small. In comparison, the data were noisy at all of the six angles for poly(PFMMD)-84 having the lowest intrinsic viscosity at low concentrations. The data for the latter polymer at 63.5 and 90° for the lowest concentration (25.64 g/L) could not be analyzed. In the range of k (or θ) where the DLS measurements were carried out, the ratio $\langle\Gamma\rangle/k^2$ was independent of k within experimental errors for all the solutions measured. The mutual diffusion coefficients D_m were obtained as $\langle\Gamma\rangle/k^2$. Typical data and fitted lines for poly(PFMMD)-56 and -85 are shown in Figure 5. The D_m obtained at different concentrations of polymer are plotted as a function of polymer concentration C (see Figures 6 and 7). For each polymer sample the data follow a straight line at low concentrations, which allows us to determine the diffusion coefficient D_0 in the dilute solution limit and the diffusion second virial coefficient k_D in eq 3. The

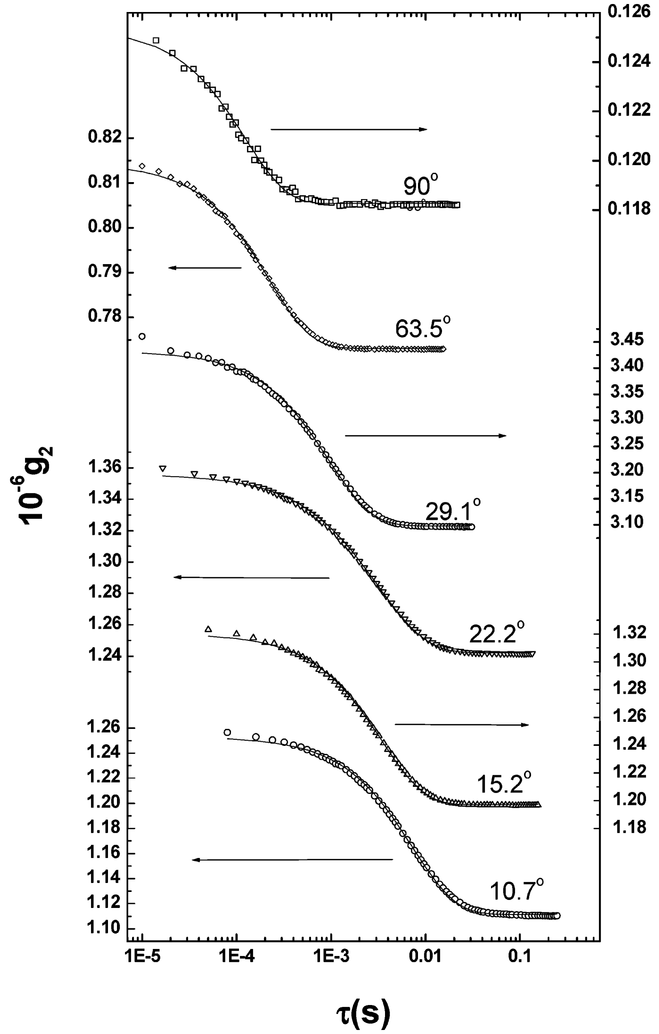


Figure 4. Light scattering intensity autocorrelation function $g_2(\tau)$ for a 25.35 g/L solution of poly(PFMMD)-56 in HFB, at scattering angles 10.7°, 15.2°, 22.2°, 29.1°, 63.5°, and 90°. Solid lines indicate the optimal fit to eq 1.

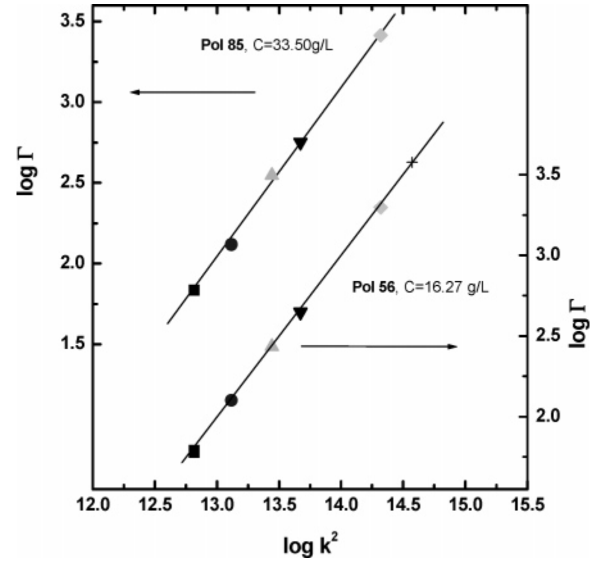


Figure 5. Logarithm of average decay rate ⟨Γ⟩, plotted as a function of the logarithm of k^2, the scattering wave vector, for polymers 56 and 85. The lines have a slope of unity.

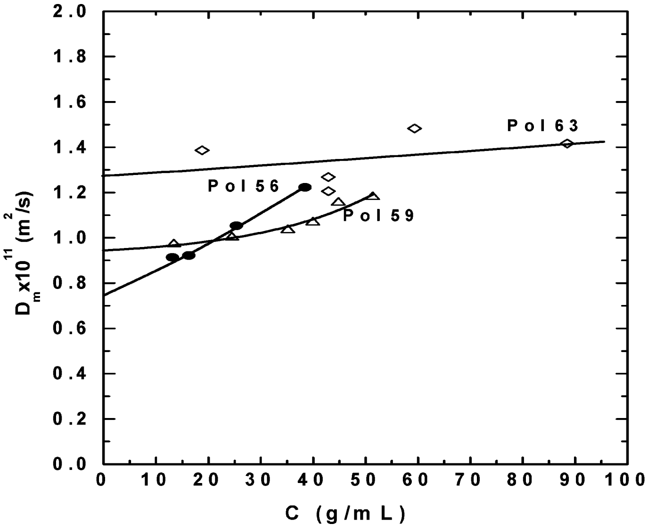


Figure 6. Mutual diffusion coefficient D_m, plotted as a function of polymer concentration C for poly(PFMMD)-56, -59, and -63 in hexafluorobenzene at 25 °C.

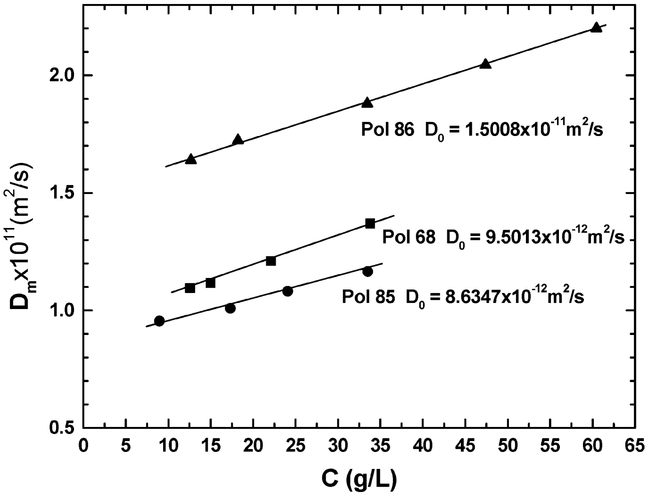


Figure 7. Mutual diffusion coefficient D_m, plotted as a function of polymer concentration C for poly(PFMMD)-68, -85, and -86 in HFB at 25 °C.

autocorrelation functions for the lowest molecular weight poly(PFMMD)-84 at concentration lower than 50 g/L were too noisy for analysis. We used the data obtained at higher concentrations to extrapolate to zero concentration. The values of D_0 and k_D thus estimated are listed in Tables 1 and 2. The hydrodynamic radius R_H was estimated from

$$R_H = k_B T/(6\pi\eta_0 D_0) \tag{6}$$

where k_BT is the thermal energy and η_0 is the solvent viscosity and is also listed in Tables 1 and 2.

The values of the hydrodynamic radius R_H give an estimate for the dimension of coils of poly(PFMMD). HFB is a thermodynamically good solvent for poly(PFMMD) based on the positive value[16] of k_D (eq 4) (Tables 1 and 2). A good linearity between D_m and C was observed for poly(PFMMD) prepared in solution (Figure 7), but the linearity was poor for the polymer prepared in bulk. The deviation from the linear dependence was pronounced for polymer 56, which we expect has a broad distribution of molecular weight.

From a fit by a power law to the relationship between the intrinsic viscosity ([η]) and hydrodynamic radius (R_H) for all of poly(PFMMD) samples characterized using DLS, we obtained $[\eta]/(\text{dL/g}) = 5.42 \times 10^{-4}(R_H/\text{nm})^{1.8\pm0.2}$. The exponent is much larger than typical

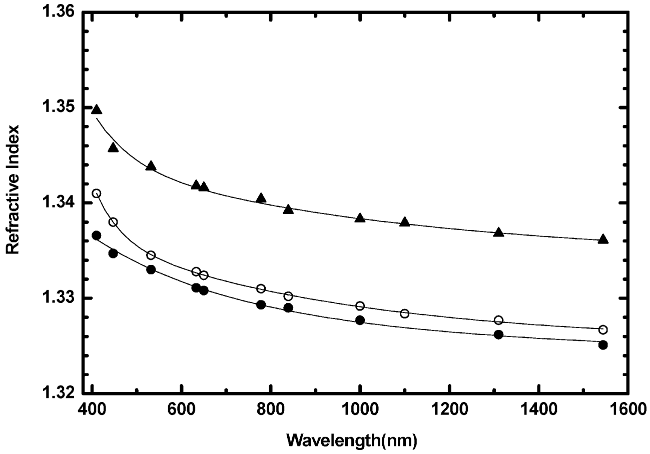


Figure 8. Refractive index dispersion of amorphous purified poly(PFMMD) (●) (film), pristine poly(PFMMD) (○) (bulk sample), and Cytop (▲) (bulk sample).

values encountered for linear monodisperse polymers in good solvents. We consider that the large exponent is due to polydispersity of the samples. It should be pointed out that the *z*-average diffusion coefficients were obtained for polydisperse samples. For samples of low intrinsic viscosity and therefore low molecular weight, meaningful signals should have been from high-molecular-weight components only, resulting in a larger hydrodynamic radius than would be expected for the polymer.

On the basis of our finding that HFB is a good solvent for poly(PFMMD)s, the molecular weights of poly(PFMMD)s were estimated from the R_H data. For that purpose, we first obtained $R_H/(\mathrm{nm}) = 1.58 \times 10^{-2}\,(M/(\mathrm{g/mol}))^{0.54}$ from literature data for polystyrene in thermodynamically good solvents such as 2-fluorotoluene,[27] benzene,[28] toluene,[29] and ethylbenzene.[30] Then, we used this equation and the measured R_H to estimate polystyrene-equivalent molecular weight. The values thus estimated are listed in Tables 1−3. Utilization of the dependence of R_H on M_w for polystyrene to estimate molecular weight of poly(PFMMD)s was justified in computer modeling. It was shown that the pendant dioxolane structural units are not congested and polymer backbone is flexible. In comparison, Cytop, used for preparation of plastic optical fibers, shows less flexibility of the polymer backbone.

Optical Properties. The refractive index of poly(PFMMD) was determined in the range of wavelength from 400 to 1550 nm. It is known that the free volume and polarizability of various functional groups in a polymer can affect its refractive index. The fluorine atom has relatively low polarizability and larger steric volume than the hydrogen atom, thus being able to lower the refractive index.[31]

Figure 8 shows measured refractive index dispersion of purified poly(PFMMD), pristine poly(PFMMD), and Cytop. Poly(PFMMD)s have a lower refractive index than Cytop does. Since densities of pristine poly(PFMMD) and Cytop are nearly the same, 2.04 and 2.03 g/mL, respectively, the difference in the refractive index is ascribed to the low polarizability of the functional groups in poly(PFMMD).

The material dispersion $M(\lambda)$ was calculated in the wavelength range including the three typical telecommunication wavelengths (810, 1310, and 1550 nm). $M(\lambda)$ was evaluated using eq 5 and is shown in Figure 9. For purified poly(PFMMD), $M(\lambda)$ approaches zero at around ~1356 nm. A sample of purified poly(PFMMD) shows the lowest pulse broadening.

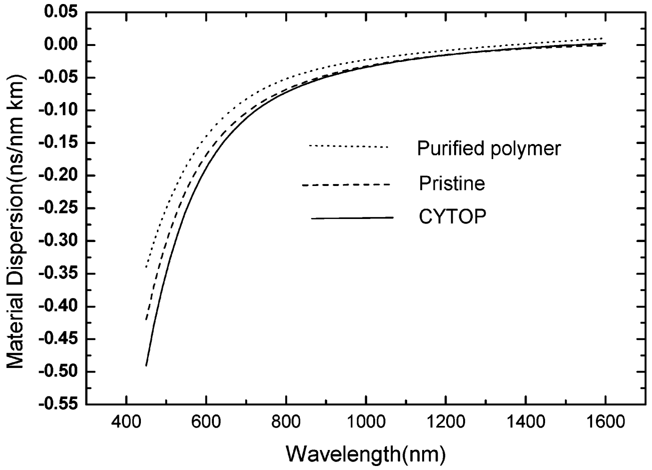


Figure 9. Material dispersion coefficient $M(\lambda)$ plotted as a function λ for pristine poly(PFMMD), purified poly(PFMMD), and Cytop.

Conclusion

The perfluoromonomer PFMMD was synthesized by a direct fluorination of the hydrocarbon precursor in liquid phase with F_2/N_2.

Polymerization of PFMMD in bulk and in the mixture with perfluoro-2-hydro-2,4-dimethyl-1,3-dioxolane and/or hexafluorobenzene was carried out by free radical mechanism using perfluorodibenzoyl peroxide and/or perfluorodi-*tert*-butyl peroxide as initiators. Polymerization afforded colorless and clear polymers with high UV−vis light transmittance. On exposure to the atmosphere the polymers become hazy. This change in the appearance of the polymer samples is most probably caused by decomposition of labile structure units formed in the course of polymerization (labile end groups arising from initiator, unstable perfluoroesters groups formed by side reaction(s) during polymerization). Based on FTIR spectra, the concentration of the −COOH groups in purified polymers is low. Carboxylic groups are probably formed by hydrolysis of perfluoroesters structural units formed in the polymers by ring-opening polymerization. The polymer produced was purified by precipitation of the HFB solution into chloroform. The purified polymer was clear and did not turn hazy upon exposure to atmosphere for a long period of time. The T_g of the purified polymers was 131−134 °C.

The molecular weight of poly(PFMMD) samples can be regulated using carbon tetrachloride, carbon tetrabromide, and sulfuryl chloride as chain transfer agents. Polymerization is characterized by nondegradative chain transfer.

Owing to a low value of the specific increment of refraction of poly(PFMMD) in HFB, the determination of the molecular weight (M_w) by static light scattering was not successful. The molecular weights of poly(PFMMD) samples have been estimated from the hydrodynamic radii determined by the dynamic light scattering. Hexafluorobenzene is a thermodynamically good solvent for poly(PFMMD). The molecular weights were estimated from dependence of the hydrodynamic radius of polystyrene polymer standards on molecular weight in thermodynamically good solvents.

The material dispersion of poly(PFMMD) samples is superior to a commercial Cytop.

Acknowledgment. The work was supported by the Japan Science and Technology Corp. through the Grant for ERATO, Koike Photonics Polymer Project. The authors thank the anonymous reviewers for their constructive comments.

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MA050085U