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Mikes Frantisek, Teng Hongxiang, Georges Kostov, B. Ameduri, Yasuhiro Koike, et al.. Synthesis and Characterization of Perfluoro-3-methylene- 2,4-dioxabicyclo[3,3,0] octane: Homo- and Copolymerization with Fluorovinyl Monomers. *Journal of Polymer Science Part A: Polymer Chemistry*, 2009, 47, pp.6571-6578. 10.1002/pola.23700 . hal-00447611

HAL Id: hal-00447611

<https://hal.science/hal-00447611>

Submitted on 15 Jan 2010

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Synthesis and Characterization of Perfluoro-3-methylene-2,4-dioxabicyclo[3,3,0] octane: Homo- and Copolymerization with Fluorovinyl Monomers

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Abstract: The synthesis of perfluoro-3-methylene-2, 4-dioxabicyclo[3,3,0] octane (D), its radical homopolymerization and copolymerization with fluoroolefins are presented.

Fluorodioxolane (D) was synthesized via direct fluorination of the corresponding hydrocarbon precursor in a fluorinated solvent by F₂/N₂ gas. It was polymerized in bulk using perfluorodibenzoyl peroxide as the initiator. The resulting homopolymer had a limited solubility in fluorinated solvents, and its glass transition temperature (T_g) was in the range of 180~190 °C. The polymeric films prepared by casting from hot hexafluorobenzene solution were transparent with low refractive index (1.329 at 633 nm). These films were thermally stable (T_d > 350 °C), and were hard and brittle. Polymerization rate of (D), in 1,1,2-trichlorotrifluoroethane, initiated by perfluorodibenzoyl peroxide at 41 °C assessed by means of ¹⁹F-NMR, was found to be

$1.77 \times 10^5 \text{ mol.L}^{-1} \cdot \text{s}^{-1}$. The copolymers of monomer (D) were prepared with fluorovinyl monomers such as chlorotrifluoroethylene (CTFE), perfluoropropyl vinyl ether (PPVE), perfluoromethyl vinyl ether (PMVE) and vinylidene fluoride (VDF). The kinetics of radical copolymerization of monomer (D) with CTFE led to the assessment of the reactivity ratios of both comonomers: $r_D=3.635$ and $r_{\text{CTFE}}=0.737$ at $74 \text{ }^\circ\text{C}$, respectively. The copolymers obtained were soluble in hexafluorobenzene and perfluoro-2-butyltetrahydrofuran, with T_g in the range of $84\text{-}145 \text{ }^\circ\text{C}$ depending on the copolymer composition. The films of the copolymers were flexible and clear with a low refractive index ($1.3350\text{-}1.3770$ at 532 nm).

KEYWORDS: Fluorodioxolane; amorphous; reactivity ratios; thermal properties; refractive index.

Introduction

Perfluorinated polymers such as Teflon AF[®], Cytop[®] and Hyflon AD[®] (Scheme 1),¹⁻³ marketed by DuPont, Asahi Glass, and Solvay Solexis, respectively, are completely amorphous cyclic polymers and contain no hydrogen atom. They exhibit remarkable properties such as a high thermal stability, an excellent near infrared transparency, and negligible absorption losses at most wavelengths. However, their preparations are complicated and costly. In addition, the glass transition temperature (T_g) of Cytop[®] is relatively low ($\sim 100 \text{ }^\circ\text{C}$). Thus, it was of interest to prepare novel perfluorinated polymers that contain a dioxolane structure to increase their amorphousness, transparency and their glass transition temperature (T_g).

(insert Scheme 1)

Our goal lies on the synthesis of various perfluoro 4- and 4,5- substituted 2-methylene-1,3-dioxolane monomers,⁴⁻⁷ and the structures of some monomers are shown in Scheme 2. These

monomers are soluble in fluorinated solvents, and readily polymerized in bulk and in solution by a free radical initiator. The polymers produced are amorphous and have glass transition temperatures (T_g) in the range of 130-160 °C. To investigate further the effect of the substitution on the properties of the 2-methylene-1,3-dioxolane monomers, a cyclopentane derivative (D in Scheme 2) was synthesized. Since a cyclopentyl group is more rigid comparing to alkyl and cyclohexyl groups, the polymer prepared from this monomer should exhibit a higher T_g than those from monomers A, B, and C.

(insert Scheme 2)

The objectives of this article deal with the synthesis of monomer D, its free radical homopolymerization and copolymerizations with various commercially available fluorinated vinyl monomers. In a second step, the physical properties of the polymers obtained have been investigated.

Experimental

Materials: Hexafluoropropylene oxide (HFPO), hexafluorobenzene (HFB), perfluoro-2-butyltetrahydrofuran (Fluorinert[®] FC-75), perfluoropropyl vinyl ether (PPVE), perfluoromethyl vinyl ether (PMVE), and vinylidene fluoride (VDF) were purchased from SynQuest, Inc. Chlorotrifluoroethylene (CTFE) was generously supplied by Honeywell. All other chemicals were obtained from Aldrich and used as received.

Methyl 3,3,3-trifluoropyruvate was prepared starting from HFPO via methyl 2,3,3,3-tetrafluoro-2-methoxypropanoate, which was transformed to methyl 3,3,3-trifluoropyruvate using sulfuric acid.⁸ Perfluorodibenzoyl peroxide (PFDBP) was prepared by reaction of pentafluorobenzoyl chloride with hydrogen peroxide.⁹ The crude product was recrystallized from

chloroform/methanol mixture (1:2 by volume). The half-life of the initiator is 10 hours at 68 °C with m.p. 76-78 °C.

Characterization: ^1H , ^{19}F , and ^{13}C NMR spectra were recorded using a Bruker ACF 300 spectrometer (300 MHz for ^1H , 75 MHz for ^{13}C measurement) or Bruker AC 400 instruments. ^{19}F NMR spectra were observed in HFB at frequency 282 MHz with fluorotrichloromethane as the standard at 60 °C in sealed NMR tubes. An insert filled with CDCl_3 or $\text{DMSO-}d_6$ was used as an internal lock. The NMR spectra of the copolymers were recorded on Bruker AC 400 instruments, using deuterated acetone as the solvent, at room temperature, and tetramethylsilane (TMS) (or CFCl_3) as the references for ^1H (or ^{19}F) nuclei. Coupling constants and chemical shifts are given in hertz (Hz) and part per million (ppm), respectively. The experimental conditions for recording ^1H [or ^{19}F] NMR spectra were as follows: flip angle 90 ° [or 30 °], acquisition time 4.5 s [or 0.7 s], pulse delay 2 s [or 2 s], number of scans 128 [or 512], and a pulse width of 5 μs for ^{19}F NMR.

FTIR spectra were obtained with a Perkin-Elmer FTIR-1600 spectrometer, accuracy $\pm 2 \text{ cm}^{-1}$.

Differential Scanning Calorimetry (DSC) measurements were carried out using a DSC 2920 module with TA Instrument 5100 system. Samples weighing 7-15 mg were placed in the pan of the DSC. The glass transition temperature (T_g) (10 °C/min) was determined as the inflection point in the endothermic jump in the second heating scan.

Thermal Gravimetric Analysis (TGA) of the polymers and salts of perfluoro-1,3-dioxolane-2-carboxylic acid was performed from room temperature to 600 °C under N_2 atmosphere using TA Instrument 5100 system with TGA module (10 °C/min).

Refractive index measurement of bulk polymer samples and films was carried out using a prism coupler (Metricon, modul 2010). The refractive indices were measured with an accuracy of 0.0005.

Kinetics of radical homopolymerization was evaluated from a decrease in the monomer concentration during polymerization monitored by ^{19}F NMR. Polymerization was carried out at 41 °C in 1,2,2-trifluoroethane (FC-113) and initiated by perfluorodibenzoyl peroxide (PFDBP). Detailed description of this procedure was previously published.¹⁰

Monomer Synthesis: The synthetic route for this monomer D is shown in Scheme 3.

(insert Scheme 3)

The cyclopentane derivative (**1** in Scheme 3) was prepared by condensation of 2-chlorocyclopentanol with methyl 3,3,3-trifluoropyruvate analogously to preparation of 2-carboxymethyl-2-trifluoromethyl-1, 3-dioxolane.⁸ Crude product was fractionally distilled, and a colorless liquid was obtained at 107 °C/17 Torr. Yield: 71%. ^1H NMR (300 MHz, d_6 -DMSO, δ ppm): 4.97 (m, 2H), 3.86 (s, 3H), 1.25-1.93 (m, 6H). ^{19}F NMR (282 MHz, d_6 -DMSO, δ ppm): -80.48- -81.10 (m, 3F).

Fluorination of **1** in a fluorinated solvent was performed using fluorine diluted with nitrogen. Solvent and low boiling byproducts were distilled off after fluorination, and the product was neutralized with aqueous potassium hydroxide. Concentrated solution of the potassium salt was treated with cold diluted sulfuric acid. Isolated crude acid was purified by fractional distillation and a colorless liquid was obtained at 106.5-109.0 °C/25 Torr. Yield: 65%. ^1H NMR (300 MHz, d_6 -DMSO, δ ppm): 6.40 (br s, 1H); ^{19}F NMR (282 MHz, d_6 -DMSO, δ ppm): -80.28- -80.94 (m, 3F); -119.33, -120.80, -122.86, -126.28, -126.96, -127.23, -127.88, -128.26, -129.38, -133.29, -134.95, -135.68, -136.56, -137.70, -138.62, -139.12, -140.01, -141.43, -142.38 (m, 8F).

The purity of the acid was confirmed by acid-base potentiometric titration. The weight per equivalent was 368 g (formula weight of the acid is 370 g/mol).

Monomer D was prepared by decomposition of dry potassium salt **2-K** with a procedure described previously⁸. According to TGA, the potassium salt started to decompose from 220 °C. Crude monomer D was isolated and washed with aqueous solution of sodium hydroxide (3%) and water. After drying with anhydrous MgSO₄, the monomer was fractionally distilled, and a colorless liquid was obtained at 85.3-86.1 °C/760 Torr. Yield: 71 %. ¹H NMR (300MHz, CDCl₃, δ ppm): None. ¹⁹F NMR (282 MHz, CDCl₃, δ ppm): -125.86 (s, F₂C=C, 2F); -126.95, -127.86, -137.82, -138.73 (dd, ¹J_{CF} = 266 Hz, ²J_{CF} = 3132 Hz, -CF₂-CF₂-CF₂-, 4F); -139.99 (s, -CF₂-CF₂-CF₂-, 2F), -129.19, -130.18, -141.70, -142.65 (dd, ¹J_{CF} = 267 Hz, ²J_{CF} = 36 Hz, -CF=, 2F). GS/MS (TIC) for C₇F₁₀O₂ (relative ratio): m/z: 306 (M⁺, 24%), 287 (M⁺-F, 8%), 212 (M⁺-F₂C=CO₂, 46%), 162 (162, 100%), 143 (24%), 93 (35%), 78 (46%), 69 (24%), 50 (35%), 31 (32%).

Polymerization: Homopolymerization of monomer D was carried out in bulk in glass ampoules initiated by perfluorodibenzoyl peroxide at 60~80 °C for 12 hrs (Table 1).

The radical copolymerizations of monomer D with various fluorovinyl monomers were performed and a typical procedure is as follows:

Monomer D (1.02 g, 3.32 mmol), t-butyl peroxyvalate (75 mg, 0.43 mmol) and 1,1,1,3,3-pentafluorobutane (3 ml) as a solvent were placed in a thick borosilicate Carius tube (length 130 mm, internal diameter 10 mm, thickness 2.5 mm). The tube was connected to a vacuum line, frozen under liquid nitrogen and purged several times by evacuation with flushing with helium. Then, CTFE (1.52 g, 13.1 mmol) was introduced into the tube from the calibrated line. D monomer/CTFE ratio in the feed was 20/80 (molar ratio). The tube was sealed under vacuum,

heated at 75 °C and shaken for 14 hours. After 14 hrs, the tube was cooled in liquid nitrogen, opened, weighed and placed in an ice-bath for 60 min. 0.55g of non-reacted CTFE were progressively released (the conversion of the monomer was 63 wt %). After precipitation from cold pentane and drying under vacuum (0.1 mmHg at 40 °C), a white powder was obtained (yield 60 wt %). The copolymer composition of D/CTFE units was 35/65 (molar ratio).

The copolymerizations of monomer D with PPVE, PMVE, and VDF were carried out similarly.

Results and Discussion

Polymerizations of monomer D were carried out under various conditions in bulk using perfluorodibenzoyl peroxide as a free radical initiator at 60~80 °C for 12 hrs. The results are summarized in Table 1. Since these polymers obtained have a limited solubility in organic solvents, including fluorinated solvents under 50 °C, it is difficult to determine their molecular weight by a size exclusion chromatography and viscosity measurement. However, we expected that the molecular weights of the polymers obtained with more initiator (samples 7 and 8) were lower than those of samples with lower initiator concentrations (samples 1-4). T_g s of the polymers obtained were in the range of 155~180 °C without purification, which are higher than those of other polyperfluorodioxolanes investigated, and were gradually decreased with the increasing concentration of the initiator due to lower molecular weights.

(insert Table 1)

To remove unreacted monomer and some oligomer, polymers obtained were dissolved in hot hexafluorobenzene and precipitated out from dichloromethane. The purified polymers have high T_g s (180-190 °C), low refractive index (1.3290 at 633 nm), and are completely amorphous and thermally stable ($T_d > 350$ °C).

The rate of the polymerization of monomer D in 1,1,2-trichlorotrifluoroethane initiated by perfluorodibenzoyl peroxide at 41 °C was determined by ¹⁹F-NMR measurements. The polymerization rate of perfluorodioxolane monomers (R_p), polymer T_g and refractive index at 633 nm are summarized in Table 2.

(insert Table 2)

As can be seen from Table 2, the mono-substituted 2-methylene-1,3-dioxolane (A) was more reactive (9-10 times) than those di-substituted monomers (D, B and C). The decrease in the reactivity of di-substituted monomers may be due to the electron withdrawing property and the steric hindrance of the perfluoroalkyl substituents. Electron density of the double bond in particular monomers may be characterized by difference between chemical shifts of $CF_2=$ and $C=$ carbon atoms in ¹³C NMR spectra. Interestingly, a linear relationship between the polymerization rate of the dioxolane monomers and the ($\delta_{CF_2=} - \delta_{C=}$) value can be noted (Figure 1).

(insert Figure 1)

The films prepared by casting from hexafluorobenzene solution were highly optical transparent, but slightly hard and brittle. It is well known that perfluoropolymers such as poly(2,2-bis(trifluoromethyl)-4,5-difluoro-1,3-dioxole and poly(2,2,4-trifluoro-5-trifluoromethoxy-1,3-dioxole) are amorphous, but they are brittle and difficult to process into final products because of poor melt flow property and low solubility in organic solvents. When they were copolymerized with tetrafluoroethylene, the resulted copolymers were flexible and processable.^{1,3} The homopolymer of the monomer D reported here was also hard and brittle. Thus, to improve the properties of the resulting polymer, the copolymerization of the monomer D with various fluorovinyl monomers such as CTFE, PPVE, PMVE and VDF were carried out (Scheme 4).

(insert Scheme 4)

To our knowledge, this is the first time that such perfluorodioxolanes have been copolymerized with aforementioned fluoroolefins. As can be seen from Table 3, monomer D content in the copolymer produced was much higher than the feeding ratio with vinyl monomers, which indicates that the dioxolane has a higher reactivity than those of these vinyl monomers.

(insert Table 3)

The ^{19}F NMR spectroscopy enables to evidence the polymer structure, which shows the characteristic multiplets ranging between -105 and -115 ppm assigned to CF_2 and CFCl groups of CTFE units in the copolymers and the wide multiples in the -125 to -135 ppm zones corresponding to the fluorinated groups of the dioxolane compound.¹¹⁻¹⁵ The absences of signals in ^1H NMR centered in the 5.2 to 6.5 ppm range and at and in the ^{19}F NMR spectra at -145 to -160 ppm range¹² assigned to $-\text{CF}_2\text{CFCl-H}$ and $-\text{CFCl-CF}_2\text{-H}$ evidences the absence of transfers to the initiator, the solvent or to moisture,

From the Kelen-Tudos method,¹⁶ the reactivity ratios of CTFE and monomer D were determined as $r_{\text{CTFE}}=0.737$ and $r_{\text{D}}=3.635$, respectively while from the Fineman and Ross theory,¹⁷ the assessment led to $r_{\text{CTFE}}=0.802$ and $r_{\text{D}}=3.945$, respectively. The typical monomer/polymer composition curve is shown in Figure 2.

(insert Figure 2)

The copolymers prepared were soluble in fluorinated solvents such as hexafluorobenzene and perfluoro-2-butyltetrahydrofuran (Fluorinert[®] FC-75), with various T_g (84-145 °C) depending on the copolymer composition and a relatively high thermal stability.

(insert Figure 3)

Figure 3 shows the T_g of monomer D/CTFE copolymer *versus* the composition of poly(CTFE-co-comonomer D) copolymers. T_g of copolymers can be generally described by the Gordon-Taylor equation:¹⁸

$$T_g = (w_1 T_{g1} + k w_2 T_{g2}) / (w_1 + k w_2)$$

where w_1 and w_2 are weight fractions of both monomeric units in the copolymer, T_g , T_{g1} and T_{g2} are the glass transition temperatures of the copolymers and of both homopolymers, respectively, and k is a fitting constant, linked to the interaction parameter. $k = 1$ means that there is no strong interactions between both monomeric units and the T_g of the copolymer should be linearly related to the weight fraction of comonomers. However, in the case of the copolymer system of D and CTFE comonomers, a plot of T_g *versus* the weight fraction of monomer D was deviating negatively from the linear relationship of the Gordon-Taylor equation. The T_g of poly(CTFE) was reported in the range of 45-60 °C.¹⁹ The result suggests that there is some repulsion between monomer D and the CTFE units due to the electronegative chlorine and fluorine substituents.

Typical IR, ¹⁹F-NMR spectra and TGA thermogram of the copolymers are shown in Figures 4-6.

(insert Figure 4)

(insert Figure 5)

(insert Figure 6)

(insert Table 4)

The refractive indexes of the copolymer films obtained by a solution casting are summarized in Table 4. These films were flexible, clear, transparent and relatively strong. Detailed mechanical and membrane properties of these copolymers are currently under investigation.

Conclusions

Perfluoro-3-methylene-2, 4-dioxabicyclo[3,3,0] octane was readily polymerized with a radical initiator. The polymers obtained are amorphous, thermal stable and has a high glass transition temperature. They are soluble in fluorinated solvent such as hexafluorobenzene. The film prepared is transparent and has low refractive index, but it is brittle and hard. The copolymers of the dioxolane monomer with perfluorovinyl monomers are prepared. They are flexible and clear and have a low refractive index.

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