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The effect of fluorine substituents on the polymerization mechanism of 2-methylene-1,3-dioxolane and properties of the polymer products

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Abstract

Perfluoro-2-methylene-1,3-dioxolane (**III**) was synthesized and polymerized with an initiator, perfluoro dibenzoyl peroxide, and a white solid product **III-P** was quantitatively isolated. The polymer was insoluble in organic solvents including fluorinated solvents such as Fluorinert FC 75 and hexafluorobenzene, but dissolved in hexafluorobenzene by heating at around 140 °C in a sealed ampoule. The X-ray measurement showed that **III-P** was semi-crystalline and melted at 230 °C. The IR spectrum of **III-P** indicated that the polymer obtained did not show carbonyl peak and it was the vinyl addition product. When the solid product was heated above the melting temperature and pressed under 100–200 kg/cm^2, we obtained an amorphous and flexible film, which is transparent from the UV region to the near IR region. The glass transition temperature was 110 °C and refractive indexes were 1.3443, 1.3434 and 1.3373 at 633, 839 and 1544 nm, respectively. The film did not degrade in concentrated sulfuric acid and aqueous sodium hydroxide solutions even heated at 80–90 °C for 2 days. The film was thermally stable and began to decompose at 300 °C under air atmosphere.

Keywords: Free radical polymerization; Perfluoro 2-methylene-1,3-dioxolane; Amorphous; Thermally and chemically stable polymer

1. Introduction

The polymerization of 2-methylene-1,3-dioxolane (**I**) and their various substituted derivatives has been widely investigated by Bailey [1,2], Klemm [3,4] and their coworkers. The free radical initiator attacks the carbon–carbon double bond at the tail position and the resulting free radical can undergo vinyl addition polymerization or ring opening as shown in Scheme 1. The ring opening isomerization and the vinyl addition step are competitive reactions; the polymerization of **I** by a free radical initiator produced a considerable amount of the ring opening product. However, substitution with fluorine atoms for the two hydrogen atoms on the methylene of **I**, 2-difluoromethylene-1,3-dioxolane (**II**) was found to readily polymerize by a free radical initiator without the ring opening isomerization [5]. In this paper, we report the preparation of perfluoro-2-methylene-1,3-dioxolane (**III**) that substitutes all hydrogen atoms of **I** with fluorine atoms.

The **III** was also readily polymerized with a radical initiator to yield vinyl addition polymer without the ring opening isomerization (Fig. 1). We described the effect of fluorine substituents of the dioxolane compound on the free radical polymerization mechanism and properties of polymers.

2. Experimental

2.1. Materials

All chemicals were purchased from Aldrich Chemical Co. or SynQuest Chemical Co. All reagents were used without further purification. Perfluoro dibenzoyl peroxide was prepared according to published procedure [6]. The crude initiator was recrystallized from petroleum ether (bp 40–60 °C), and purified initiator has a melting point of 76–78 °C; its half-life at 68 °C is 10 h [7].

2.2. Instrumentation

^{19}F, ^{1}H and ^{13}C NMR spectra were obtained on Bruker AC-300 spectrometer in $CDCl_3$ containing 0.03% (v/v) TMS as an

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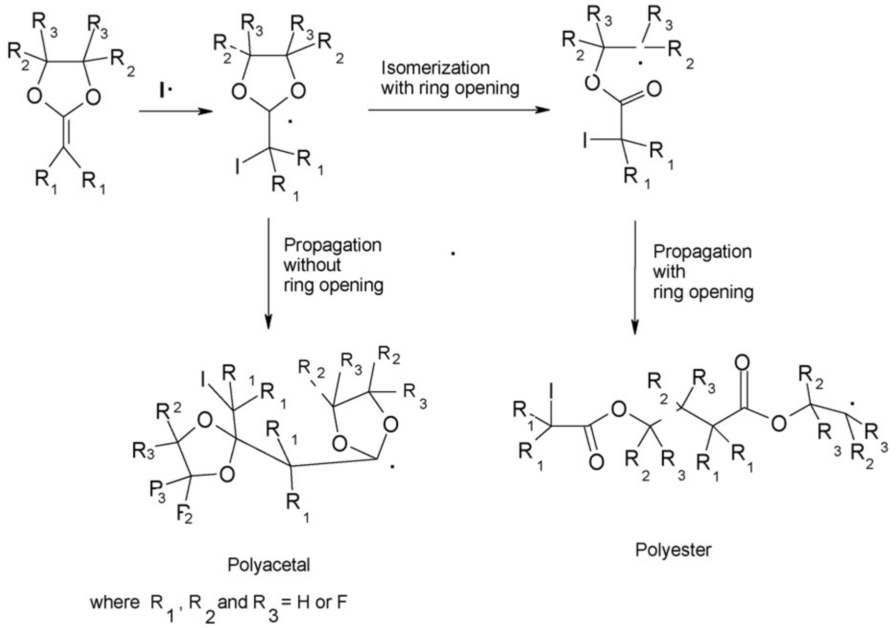


where R_1, R_2 and R_3 = H or F

Scheme 1. Free-radical polymerization mechanism of the dioxolanes with or without ring opening.

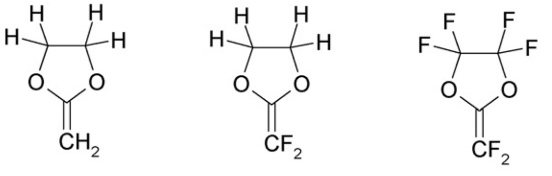
internal reference. The IR spectra were measured on a Perkin-Elmer 1600 series FTIR. GC–MS measurements were conducted using a 5970 series by Hewlett-Packard Co. The refractive indexes of the polymer were measured using a Merticon model 2010 prism coupler made by Metricon Corp. Thermal properties were determined using a TA Instruments Inc. DSC 2920 differential scanning calorimeter and a Hi-Res Modulated TGA 2950 thermogravimetric analyzer. Wide angle X-ray experiments were performed by using a Rigaku RINT 2500 V diffractometer with graphite monochromatized Cu Kα_1 radiation. The intensities were recorded on a square image plate of a size of about 130 cm^2. The measurements were carried out for unoriented samples at room temperature.

2.3. Monomer preparation

2.3.1. Preparation of perfluoro-2-methylene-1,3-dioxolane (*III*)

Methyl 2-methyl-1,3-dioxolane-2-carboxylate (**3a**) was prepared by condensation of ethylene glycol (**1**) (372 g, 6 mol) with methyl pyruvate (**2a**) (612 g, 6 mol) in the presence of *p*-toluenesulfonic acid (40 g, 0.23 mol) in benzene (1200 ml) (Scheme 2).

Water produced was distilled out as azeotropic mixture with benzene using Dean–Stark adapter. The remaining reaction mixture was washed with saturated aqueous solution of sodium bicarbonate, with water and dried using anhydrous magnesium sulfate. After removing benzene using Vigreux column, pure dioxolane ester was obtained by fractional distillation in 32% yield. Bp 85–87 °C, ^{1}H NMR (δ ppm, DMSO-d_6): 4.07 (d, –CH_2–CH_2–, 4H), 3.77 (s, –$COOCH_3$, 3H), 1.60 (s, –CH_3, 3H). The yield of **3a** was found to be low, thus we have alternatively prepared **3b**.



I **II** **III**

Fig. 1. Chemical structures of dioxolane compounds investigated.

The ester **3b** was prepared by the condensation of **1** (372 g, 6 mol) with 2-oxopropyl acetate (**2b**) (696 g, 6 mol) and work up of the reaction mixture was carried out analogously to aforementioned procedure. **3b** was obtained in yield 68%.

Bp 97–98 °C/17 Torr, ^{1}H NMR (δ ppm, $CDCl_3$): 4.27 (s, –CH_2–, 2H), 4.00 (d, –CH_2–CH_2–, 4H), 2.08 (s, –$COCH_3$, 3H), 1.40 (s, –CH_3, 3H).

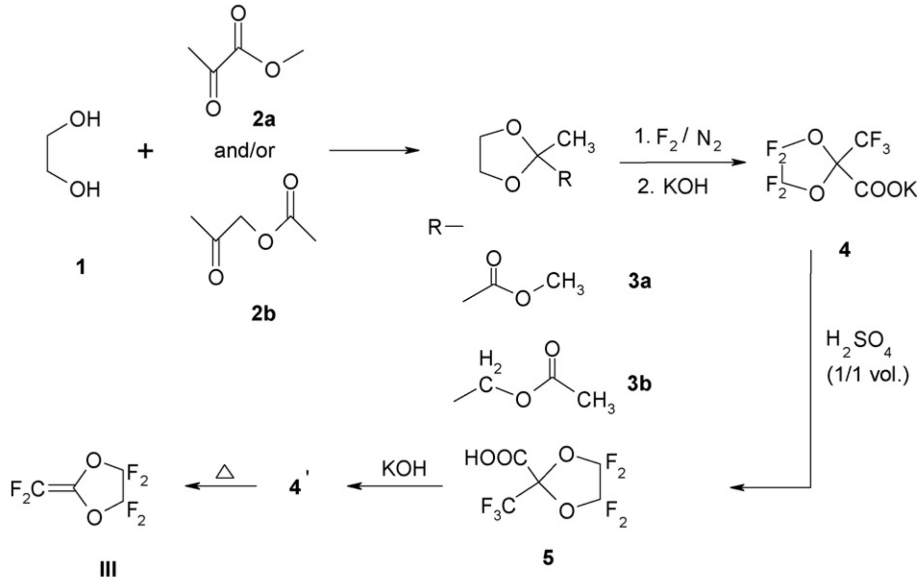
Since the fluorination and following work up of **3a** and **3b** produce the same carboxylic compound, we have carried out the fluorination of the mixture of **3a** and **3b**. Fluorination of the mixture of **3a** (959 g, 6.57 mol) and **3b** (1488 g, 9.30 mol) was carried out in a fluorinated solvent using F_2/N_2 mixture as described before [8,9]. The fluorinated product was neutralized by aqueous solution of potassium hydroxide.

Pure acid **5** was obtained by fractional distillation (25% yield). Bp 96–98 °C/97 Torr, ^{1}H NMR (δ ppm, DMSO-d_6): 9.60 (–COOH); ^{19}F NMR (δ ppm, DMSO-d_6): −81.41 (3F, –CF_3), −81.73, −82.18, −82.66, −83.10 (4F, –CF_2–CF_2–).

The purity of the acid **5** produced was confirmed by acid–base potentiometric titration. The weight per equivalent was 257.2 g (formula weight of the acid is 258.06 g/mol).

Pure potassium salt of 4,4,5,5-tetrafluoro-2-trifluoromethyl-1,3-dioxolane-2-carboxylic acid (**4′**) was prepared by neutralization of aqueous solution of acid **5** with aqueous potassium hydroxide solution and dried.

Monomer **III** was prepared by thermal decomposition of salt **4′**. Potassium salt **4′** starts to decompose according to TGA at



Scheme 2. Synthetic route for **III**.

200 °C. Decomposition was carried out using procedure described previously [9,10].

The **III** was purified by fractional distillation having bp 21.5 °C under atmospheric pressure. Structure of **III** obtained was confirmed by ^{19}F and ^{13}C NMR spectroscopy.

^{19}F NMR (in $CDCl_3$): −89.04, −89.05, −89.06 ($–CF_2–CF_2–$, 4F), −127.65, −127.66, −127.67, −127.68 ($=CF_2$, 2F).

^{13}C NMR (in $CDCl_3$): 142.67 (tp, $^1J_{CF} = 272.42$ Hz, $^5J_{CF} = 2.30$ Hz, $CF_2=$), 131.27 (tm, $^2J_{CF} = 46.55$ Hz, $^4J_{CF} = 3.45$ Hz), 122.93, 122.91, 122.48, 122.45, 121.98, 119.31, 119.29, 118.80, 118.32, 115.65, 115.63, 115.18, 115.14, 114.72, 114.70, 114.69 ($–CF_2–CF_2–$).

2.4. Polymerization

Monomer **III** was polymerized in bulk or in hexafluorobenzene solution using a free radical initiator perfluoro dibenzoyl peroxide, because 2,2′-azobisisobutyronitrile (AIBN) is not soluble in **III**. Polymerization of **III** was carried out in most cases in glass ampoules.

2.4.1. Bulk polymerization

Glass ampoules were charged with mixture of monomer **III** and initiator and sealed after repeating of three times cycle freeze–pump–thaw. In a typical polymerization experiment, the mixture of monomer **III** (10 g) and perfluoro dibenzoyl peroxide (30 mg) in a sealed glass ampoule was heated at 60 °C for 48 h. Polymer was washed with chloroform and after drying the solid under vacuum at 40 °C, 9.2 g of solid material was obtained.

2.4.2. Polymerization in hexafluorobenzene

The hexafluorobenzene solution (30 ml) of **III** (10 g) and perfluoro dibenzoyl peroxide (30 mg) were degassed, sealed in glass ampoule and heated at 60 °C. After several hours, a solid product started to precipitate and the solution was heated continuously for 40 h. The solid product was isolated, washed with chloroform and dried (9.0 g). Polymer **III-P** was not soluble in any organic solvents including hexafluorobenzene and FC-75 at 60–80 °C. However, the polymer is soluble at 140–150 °C in hexafluorobenzene in a sealed ampoule. IR spectra of **III-P** showed that there were no carbonyl peaks at around 1750–1800 cm^{-1}. The polymer produced was semi-crystalline and melted at 230 °C.

3. Results and discussion

When the non-fluorinated monomer **I** was polymerized by a free radical initiator, AIBN at 60 °C, the ring opening product was produced as much as 50%, which indicates that the rates of the ring opening isomerization and propagation of the vinyl addition polymerization were almost the same [1,2]. However, Zhu and Pittman reported that when **I** was polymerized by an activated carbon supported sulfuric acid (a cationic polymerization), the vinyl addition product was obtained quantitatively [11]. The solid product was found to be insoluble in common solvents and had a substantial degree of crystallinity. They suggested that the polymer produced was a linear structure and the chains could pack tightly giving a high cohesive energy density. We have previously found the difluoro polymer (**II-P**) obtained by the free radical initiator, AIBN, was insoluble in common organic solvents such as DMSO, THF, chloroform and toluene, but was soluble in fluorinated solvents such as hexafluoro 2-propanol, trifluoroacetic acid (TFA) or mixed solvent of chloroform and TFA [5]. IR and NMR spectra of **II-P** indicated that the polymer obtained was mainly the vinyl addition product. The powder X-ray diffraction pattern indicated that polymer was semi-crystalline and its melting point was 355 °C, which was higher than that of Teflon® (329 °C). The glass transition of **II-P** was 125 °C and thermal decomposition began at 427 °C under nitrogen and at around 414 °C under an air atmosphere. The polymer did not degrade in 20% aqueous sulfuric acid and 30% aqueous sodium hydroxide solutions at 60 °C over 2 days.

The **III** was found to be readily polymerized in bulk or in hexafluorobenzene using perfluoro dibenzoyl peroxide as an initiator at 60–80 °C. The white solid product was quantitatively isolated. The polymer **III-P** did not dissolve in any organic solvents, including fluorinated solvents at 60–80 °C, but was soluble in hexafluorobenzene by heating around 140–150 °C in a sealed ampoule. IR spectrum of **III-P** showed that there were no carbonyl peaks. As we have described for **II-P** [5], the monomer **II** yielded the vinyl addition product. The X-ray measurement showed that **III-P** was semi-crystalline (Fig. 2A) and melted at 230 °C. When the solid product was heated above the melting point (250 °C) and pressed under 100–200 kg/cm^2, it became an amorphous flexible film (Fig. 2B) and consequently transparent from the UV to the near IR regions. The glass transition temperature was 110 °C (Fig. 3). We have measured the refractive indexes of the polymer at various wavelengths and were found to be 1.3443, 1.3434 and 1.3373 at 633, 839 and 1544 nm, respectively. These wavelengths are commonly used in telecommunication. The refractive indexes of **III-P** are similar to the values of Cytop$^{®}$ which is transparent amorphous perfluoro polymer.

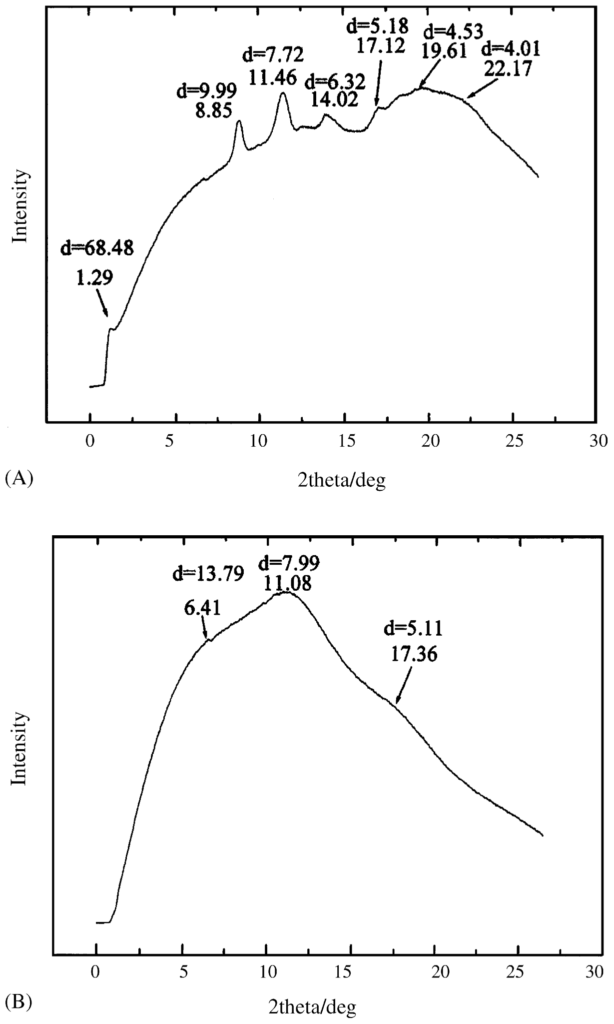


Fig. 2. (A) X-ray data of **III-P** as obtained and (B) X-ray data of **III-P** after heating and compress molding at 250 °C.

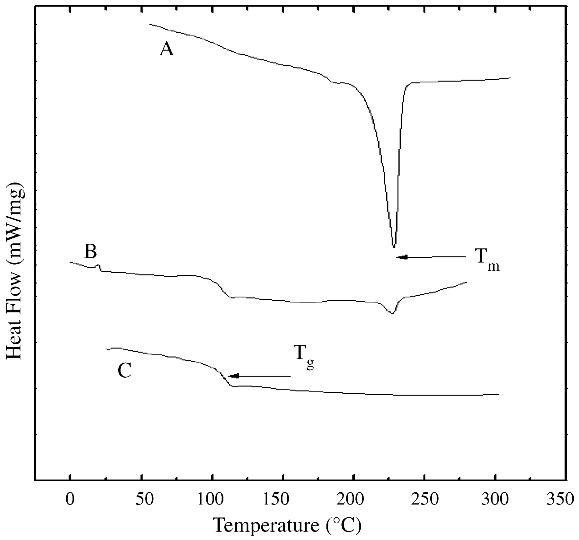


Fig. 3. Differential scanning calorimetry (DSC) trace of **III-P**: (A) **III-P** as obtained (first scan), (B) the second DSC scan of the **III-P** sample after heating to 300 °C and (C) the third DSC scan of the sample B.

The films were not degraded in concentrated sulfuric acid and aqueous sodium hydroxide solutions even when heated at 80–90 °C for 2 days. The polymer obtained was thermally stable and began to decompose at around 300 °C under an air atmosphere (Fig. 4).

We argue that when fluorine atoms are present on the outer positions of the methylene of **I**, the vinylidene group is then polarized. Therefore, the vinyl addition in the polymerization may be more favorable for **II** and **III** in comparison with the hydrocarbon analogue **I**. The transition state in the polymerizations of **II** and **III** involves a relatively electrophilic radical species and a relatively nucleophilic double bond. Consequently, the propagation reaction through vinyl addition is appreciably faster than the isomerization and results in a polymer without a ring opening product [12].

The polymers **II-P** and **III-P** have a substantial degree of crystallinity and a similar linear polymer structure as the polymer

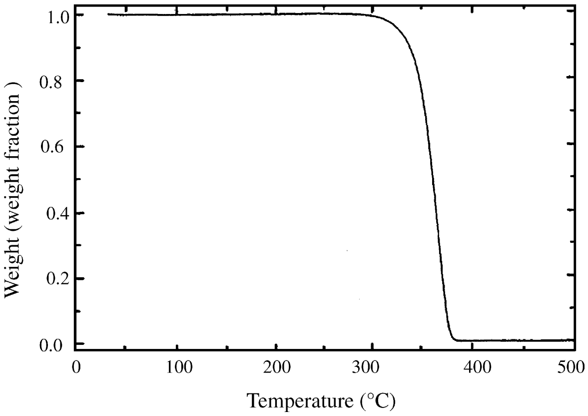


Fig. 4. Thermogravimetric analyses (TGA) trace of **III-P** sample under an air atmosphere.

product obtained by a cationic polymerization of **I**. Therefore, the polymer chains can pack tightly, giving a high cohesive energy density. **II-P** was heated over the melting point, but remained crystalline upon cooling. However, **III-P** has a considerably lower melting point (230 °C) in comparison with **II-P** (355 °C) and when it was heated over 230 °C, the crystallinity disappeared and an amorphous product was isolated. This phenomenon is currently being investigated further.

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