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Investigation of homopolymerization rate of perfluoro-4,5-substituted-2-methylene-1,3-dioxolane derivatives and properties of the polymers

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Abstract

Five perfluoro-4,5-substituted-2-methylene-1,3-dioxolane monomers were synthesized. These monomers were found to readily polymerized by a free radical initiator in bulk and/or in solutions. Homopolymerization rates were determined using in situ ^{19}F NMR measurements and found to be 0.25 to 1.66×10^{-4} mol L^{-1} s^{-1} in 1,1,2-trichlorotrifluoroethane at 41 °C using the perfluorodibenzoyl peroxide as an initiator. The rates depend on the substituents on the 4 and 5 positions of the dioxolane. The purified polymers were thermally stable (up to 350 °C). They show low refractive indexes (1.33–1.36 at 532 nm). They are transparent from UV to near IR region and have high glass transition temperatures (100–170 °C).

Keywords: Perfluoro-4,5-substituted-2-methylene-1,3-dioxolane; ^{19}F NMR spectra; Polymerization rate; Polymer properties

1. Introduction

Amorphous perfluorinated polymers have many potential applications as opto-electronic materials due to their low refractive index as well as chemical and thermal stability [1,2]. We have synthesized various perfluoro-4,5-substituted-2-methylene-1,3-dioxolane compounds. These monomers are soluble in fluorinated solvents and readily polymerized in bulk and in solution by a free radical initiator. The polymerization process involves vinyl additional mechanism. In order to investigate the effect of the 4,5-substitutions on the perfluoro-1,3-doxolane, we have determined the homopolymerization rate of these dioxolane monomers in fluorinated solvents using in situ ^{19}F NMR spectroscopy.

2. Experimental

2.1. Materials

All chemicals were purchased from Aldrich Chemical Co. and used without further purification. Perfluorodibenzoyl peroxide (FBPO) was prepared according to published procedure [3]. After recrystallization from petroleum ether (bp 40–60 °C), the pure initiator has melting point of 76–78 °C and the half-life is 10 h at 68 °C [4].

2.2. Instrumentation

2.2.1. ^{1}H, ^{19}F and ^{13}C NMR spectra

^{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 of 282 MHz with fluorotrichloromethane as a standard. Unless otherwise stated, $CDCl_3$ or DMSO-d_6 was used for field lock.

2.2.2. FTIR spectra

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

2.2.3. GC–MS analyses

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

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2.2.4. Differential scanning calorimetry (DSC)

A DSC 2920 module with TA Instrument 5100 system was used for the glass transition temperature (T_g) measurements, and the samples (7–15 mg) were used for the measurement. The T_g at heating rate of 10 °C/min was determined as an endothermic shift in the second heating scan.

2.2.5. Refractive index measurements

The polymer films (0.1–0.2 mm thick) fabricated by casting their hexafluorobenzene (C_6F_6) solutions on glass plates were used to measure the refractive index. A prism coupler (Metricon, modul 2010) was utilized. The measurement accuracy was ±0.0005. The probe wavelengths in the prism were 532, 632, 839 and 1544 nm.

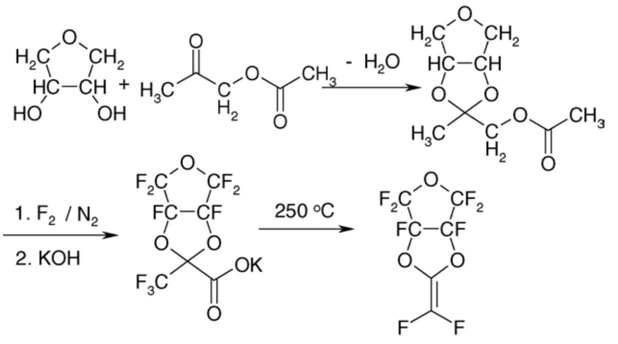
2.3. Synthesis of perfluoro-4,5-substituted-2-methylene-1,3-dioxolanes (the chemical structures are shown in Fig. 1)

2.3.1. Preparation of perfluoro-2-methylene-furo [3,4-d][1,3] dioxolane (A) and its polymer

Monomer A was prepared via the decarboxylation of the potassium salt, which was synthesized by the route described in Scheme 1.

2.3.1.1. Preparation of 1,4-anhydroerythritol. *cis*-1,4-Anhydroerythritol was prepared according to the published procedure [5]. bp 105–107 °C/0.2–0.5 Torr. ^{1}H NMR (in $CDCl_3$) δ (ppm): 4.2 (m, –CH–, 2H), 3.6–4.0 (m, $–CH_2–$, 4H), 3.8 (s, –OH, 2H).

2.3.1.2. Preparation of $CH_3COCH_2OOCCH_3$. Acetyl chloride (721 g, 9 mol) was added dropwise at 0 °C to a flask charged with pyridine (719 g, 9 mol), hydroxyacetone (90% of purity, 741 g, 9 mol) and 2 L of ether. After addition, the reaction mixture was stirred for 2 h at room temperature. The pyridine salt was removed by filtration. After the ether was evaporated, the remained oil was distilled under reduced pressure. Pure product (971 g) was obtained (bp 80–95 °C/40 Torr) in 93% of yield. ^{1}H NMR (in $CDCl_3$) δ (ppm): 4.65 (s, $–CH_2–$, 2H), 2.15 (s, two $–CH_3$, 6H). Anal. calcd. for $C_5H_8O_3$: C, 51.72, H, 6.90. Found: C, 51.50, H, 6.96.



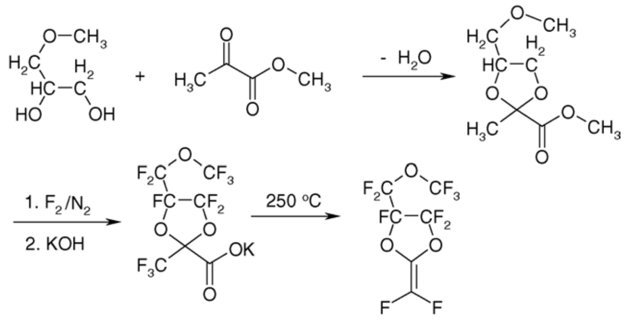
Scheme 1. Synthetic route of monomer A.

2.3.1.3. Preparation of ketal. The ketalization reaction was performed between 1,4-anhydroerythritol and 2-oxopropyl acetate. 1,4-Anhydroerythritol (448 g, 4.3 mol), 2-oxopropyl acetate (500 g, 4.3 mol), *p*-toluene sulphonic acid (30 g) and 1 L of benzene were placed into a 2 L flask equipped with a Dean-Stark trap. The mixture was refluxed until 78 mL of water was distilled out. The product was neutralized using 30 g of sodium carbonate, and then washed with 1 L of water. Distillation gave 624 g (3.09 mol) of pure product in 71% yield (bp 130 °C/8 Torr). ^{1}H NMR (in $CDCl_3$) δ (ppm): 4.8 (s, $–CH_2OCO–$, 2H), 4.16, 4.05, 4.01 (s, $–CH_2–$, 4H), 3.5–3.3 (m, –CH–, 2H), 2.11 (s, $–OCCH_3$, 3H), 1.34, 1.48 (s, $–CCH_3$, 3H). Anal. calcd. for $C_9H_{14}O_5$: C, 53.47; H, 6.93. Found: C, 53.60; H, 6.82.

2.3.1.4. Fluorination of ketal. The ketal (1000 g, 4.95 mol) was directly fluorinated in fluorinated solvent using F_2/N_2 [6,7]. The reaction mixture was then neutralized with cold aqueous KOH solution, and organic and water phases were separated. The water in aqueous phase was distilled out under reduced pressure. A 1295 g (3.46 mol) of potassium salt was obtained in 70% yield after drying at 80 °C under vacuum. ^{1}H NMR (in d_6-DMSO): none; ^{19}F NMR (in d_6-DMSO) δ (ppm): −82, −80.05 (3F, CF_3), −78.57, −79.92, −81.58, −91.32 (4F, $–OCF_2–$), −129.58, 130.79 (m, 2F, –CFO–).

2.3.1.5. Decarboxylation of the potassium salt. The potassium salt (100 g, 0.267 mol) was decomposed at 250 °C under an argon stream. The product was collected in a trap cooled at −78 °C. Fractional distillation gave 36.3 g (0.134 mol) of pure monomer (bp 74 °C/760 Torr) in 50% of yield. ^{1}H NMR (in $CDCl_3$): none; ^{19}F NMR (in $CDCl_3$) δ (ppm): −79.66(dm), −90.72 (dm, 4F, $–OCF_2–$), −126 (t, 2F, $=CF_2$, $^{5}J_{F–F} = 3.09$ Hz), −136.20 (dm, 2F, –CFO–, $^{3}J_{F–F} = 17.53$ Hz); ^{13}C NMR (in $CDCl_3$) δ (ppm): 118.2 (dddd, $–OCF_2–$, $^{1}J_{C–F} = 273.11$ Hz, $^{1}J_{C–F} = 239.38$ Hz, $^{2}J_{C–F} = 37.59$ Hz, $^{3}J_{C–F} = 4.97$ Hz), 137.99 (t, =C, $^{2}J_{C–F} = 45.33$ Hz), 142.8 (tt, $=CF_2$, $^{4}J_{C–F} = 2.21$ Hz, $^{1}J_{C–F} = 273.11$ Hz), 109.50 (dm, –CFO–, $^{1}J_{C–F} = 274.77$ Hz). GC–MS: *m*/*e* 272 (M^+).

2.3.1.6. Free radical polymerization of monomer A in bulk. A glass tube charged with 2 g of monomer A and 8.8 mg of perfluorodibenzoyl peroxide was sealed after three freeze-pump-thaw cycles. After polymerization at 60 °C for 1 day, a solid polymer bar was obtained. The polymer was dissolved in C_6F_6, and then precipitated into chloroform. The collected polymer was dried to constant weight (1.8 g) and the yield was 90%. The intrinsic viscosity of the polymer in C_6F_6 at 25 °C was 25 mL/g. FTIR: no carbonyl group absorption. ^{19}F NMR (dissolved in C_6F_6 and using an insert filled with $CDCl_3$ for field lock) δ (ppm): −132 (2F, –CF–), −110 (2F, $–CF_2–$ in the main chain), −80, −95 (4F, $–CF_2–$ in the ring). DSC: T_g was 168 °C. TGA: initial decomposition temperature was 355 °C under nitrogen atmosphere. Refractive indexes were: 1.3572, 1.3548, 1.3515 and 1.3502 at 532, 633, 839 and 1544 nm, respectively.



Scheme 2. Synthetic route of monomer C.

2.3.2. *Preparation of perfluoro-2-methylene-4-methyl-1,3-dioxolane (B) and its polymers*

Monomer B and its polymers were prepared in our laboratory that was previously reported [8].

2.3.3. *Preparation of perfluoro-2-methylene-4-methoxymethyl-1,3-dioxolane (C) and its polymer*

Monomer C was prepared according to the following synthetic route described in Scheme 2.

2.3.3.1. Preparation of ketal. The mixture of 3-methoxy-1,2-propane-diol (2 mol, 212 g), methyl pyruvate (2 mol, 204 g) ion-exchange resin (H form, DOWEX®) (10 g) and benzene (1 L) was charged into a flask equipped with a Dean-Stark trap and refluxed until the evolution of water ceased (around 38 mL water). Fractional distillation gave 209 g of pure methyl 4-methoxymethyl-2-methyl-1,3-dioxane-2-carboxylate (bp 80 °C/1 Torr) in 55% yield. ^{1}H NMR (in $CDCl_3$) δ (ppm): 1.60 (d, 3H, $–CH_2OCH_3$), 4.2–4.5 (m, 1H, –OCH–), 4.12–4.25 and 3.8–3.9 (m, 2H, $–OCH_2–$ in the ring), 3.76 (d, 3H, –COOCH3), 3.41–3.6 (m, 2H, $–OCH_2–$ in the side chain), 3.39 (d, 3H, CCH_3). Anal. calcd. for $C_8H_{14}O_5$: C, 50.53, H, 7.37. Found: C, 51.10, H, 7.44.

2.3.3.2. Fluorination of ketal. Methyl 4-methoxymethyl-2-methyl-1,3-dioxane-2-carboxylate (650 g, 3.42 mol) was also fluorinated in fluorinated solvent using F_2/N_2. The reaction mixture was neutralized with cold aqueous KOH solution. Potassium salt (780 g, 2.56 mol) was obtained in 75% yield. ^{1}H NMR (in d_6-DMSO): none; ^{19}F NMR (in d_6-DMSO) δ (ppm): −55.11 (dt, 3F, $–OCF_3$), −76.59 and −81.00 (2F, $–OCF_2C$), −82, −80.05 (3F, $–CCF_3$), −85.35 (m, 2F, $–OCF_2O–$),−120.67 (dm, 1F, –OCFC–).

2.3.3.3. Decarboxylation of the potassium salt. The potassium salt (100 g, 0.243 mol) was decomposed at 250 °C under an argon stream. The product was collected in a trap cooled at −78 °C. Fraction distillation gave 61 g (0.194 mol) of pure monomer (bp 67 °C/760 Torr) in 81% yield. ^{1}H NMR (in $CDCl_3$): none; ^{19}F NMR (in $CDCl_3$) δ (ppm): −55.56 (dt, 3F, $–OCF_3$), −82.54 and −87.40 (2F, $–OCF_2C$), −85.28 (m, 2F, $–OCF_2O–$),−128.29 (s), −128.74 (s), 129.59 (m), 130.04 (m) (2F, $CF_2=$), −130.66 (m, 1F, –OCF–). GC–MS: *m/e* 310 (M^+).

2.3.3.4. Free radical polymerization of monomer C in bulk. A glass tube charged with 4 g of monomer C and 20 mg of perfluorodibenzoyl peroxide was sealed after three freeze-pump-thaw cycles. After polymerization at 60 °C for 1 day, a solid polymer bar was obtained. The polymer was dissolved in C_6F_6, and then precipitated into chloroform. The collected polymer was dried to constant weight (3.5 g) and the yield was 88%. The intrinsic viscosity of the polymer in C_6F_6 at 25 °C was 28 mL/g. FTIR: no carbonyl group absorption. ^{19}F NMR (dissolved in C_6F_6 and using insert filled with $CDCl_3$ for field lock) δ (ppm): −58.32 (3F, $–OCF_3$), −79.40 (2F, $CF_3OC\boldsymbol{F}_2–$), −85.8 (2F, $–CF_2–$ in the ring), −109.05 (2F, $–CF_2–$ in the main chain), −121.8 (1F, –CF– in the ring). DSC: T_g was 101 °C. TGA: initial decomposition temperature was 366 °C under nitrogen atmosphere. Refractive indexes: 1.3328, 1.3301, 1.3264 and 1.3233 at 532, 632, 839 and 1544 nm, respectively.

2.3.4. *Perfluoro-2-methylene-4,5-dimethyl-1,3-dioxolane (D) and perfluoro-3-methylene-2,4-dioxabicyclo [4,3,0] nonan (E)*

Monomer D and monomer E were prepared in our laboratory and previously reported [9]. The ratio of the *cis* and *trans* of the fluorine atoms on the 4 and 5 positions of monomer D was found to be 2.9:1.

3. Results and discussion

The chemical structures and ^{19}F NMR spectra of perfluoro-4,5-substituted-2-methylene-1,3-dioxolanes investigated are shown in Figs. 1 and 2.

These monomers are soluble in fluorinated solvents such as 1,2,2-trifluorotrichloroethane (FC-113) and α,α,α-trifluorotoluene, while the polymers produced are not soluble in these two solvents. Though polymers were produced throughout the polymerizations, only resonances from monomers were observed in

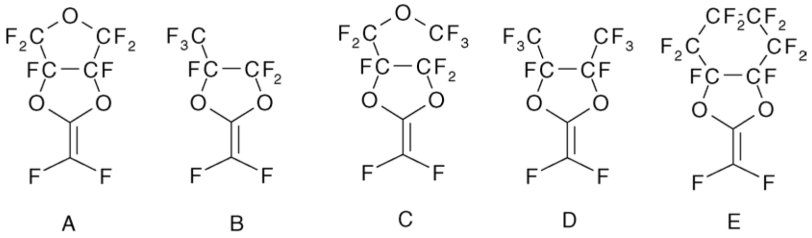


Fig. 1. Chemical structures of perfluoro-4,5-substituted-2-methylene-1,3-dioxolane derivatives.

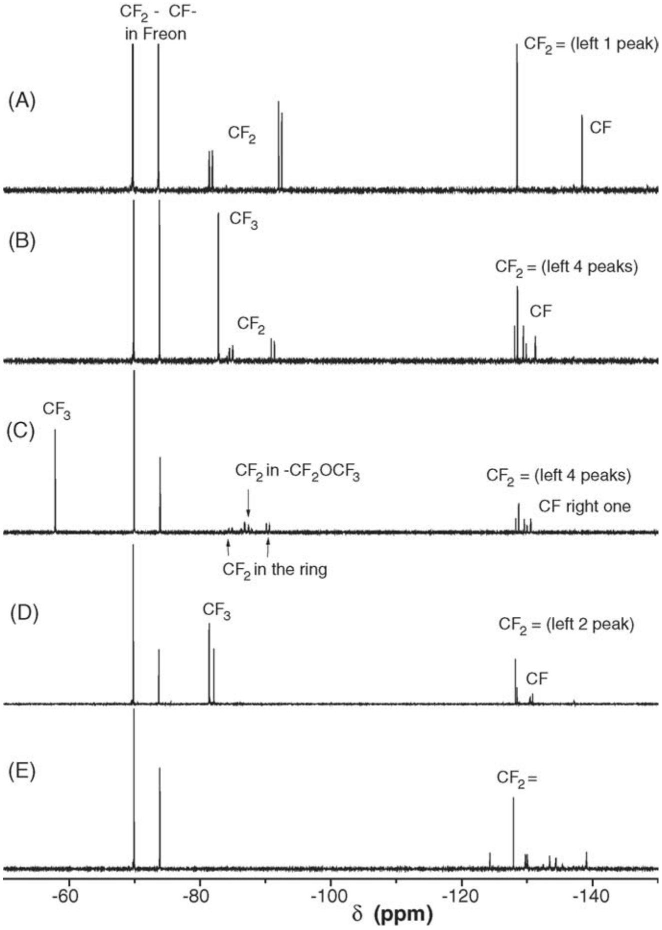


Fig. 2. The ^{19}F NMR spectra of FC-113 solutions of perfluoro-2-methylene-4,5-substituted-1,3-dioxolane derivatives.

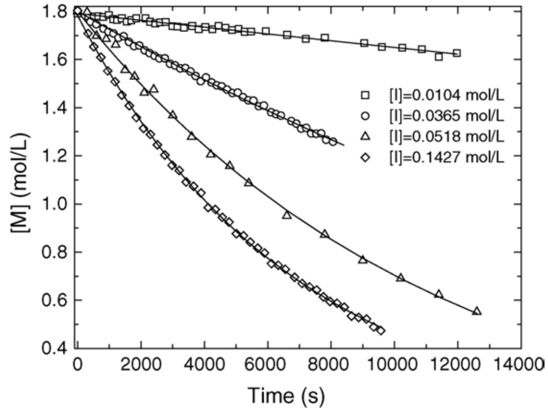


Fig. 4. Monomer concentrations vs. the polymerization time for monomer A. Initial monomer concentration: 1.8 mol L^{-1}, solvent: FC-113, initiator: perfluorodibenzoylperoxide, polymerization temperature: 41 °C.

the ^{19}F spectra, as shown in Fig. 3. Thus, it is possible to follow the concentration of monomers during the polymerization. Two fluorine atoms attached to the vinylidene group $CF_2=$ for the dioxolane monomers were utilized to calculate the monomer concentration during the polymerization. ^{19}F signals corresponding to the $CF_2=$ group for the monomers A–E appear in the range of −120 to −130 ppm and the signal for $CFCl_2$ of FC-113 is a triplet at −73.62 ppm. For α,α,α-trifluorotoluene, a resonance signal corresponding to $-CF_3$ appears at −65.38 ppm. The solution of a dioxolane monomer in FC-113 and perfluorodibenzoylperoxide as a free radical initiator were placed into a NMR tube, which contains a sealed ampoule filled with d_6-DMSO as a field locker. After replacing air with argon in the NMR tube, the tube was sealed and placed into a NMR apparatus thermostated at 41 °C. The instantaneous monomer concentration was computed from the ratio of the integral of the peak for $CF_2=$ to the resonance for $CFCl_2-$ of FC-113. For each measurement, 50 scans were accumulated and the resulting data point was assigned the time corresponding to the time from the beginning to the polymerization to the end of the measurement. The polymerization rate, $R_p = d[M]/dt$ for monomers A–E was measured by varying the concentrations of the monomer and initiator. As seen from Fig. 4, the polymerization rates were greatly enhanced with increasing the initiator concentration.

This is a typical trend of a free radical polymerization of a vinyl monomer [10]. The conversion of monomers A–E versus polymerization time using the same initiator concentration were measured and are shown in Fig. 5. The initial polymerization rates, R_p for these monomers were summarized in Table 1.

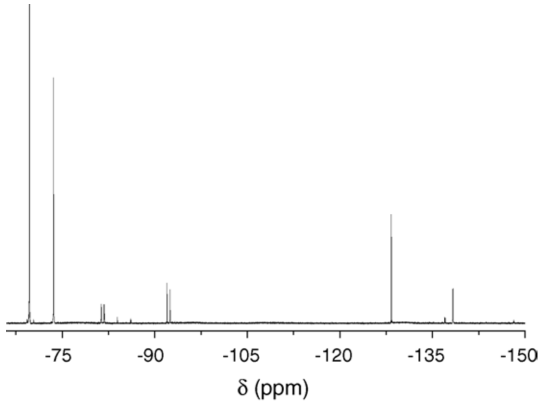


Fig. 3. ^{19}F NMR spectrum of monomer A at 60% conversion. Initial monomer concentration: 1.8 mol L^{-1}, solvent: FC-113, initiator: perfluorodibenzoylperoxide, polymerization temperature: 41 °C.

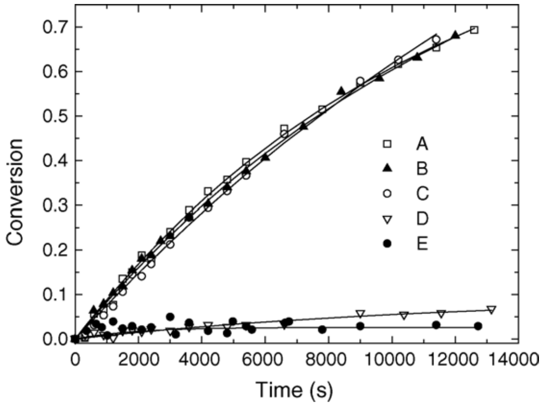


Fig. 5. Monomer conversion vs. the homopolymerization time in FC-113 initiated by perfluorodibenzoyl peroxide (0.05 mol L^{-1}) at 41 °C. The initial concentrations for all monomers were 1.8 mol L^{-1}.

Table 1
Polymerization rates, glass transition temperature and refractive index of monomers A–E[a]

Monomer	A	B	C	D	E
Rate R_p ($\times 10^4$ mol L^{-1} s^{-1})	1.66	1.56	1.40	0.15	0.25
T_g (°C)	168	135	101	165	165
Refractive index at 632 nm	1.3572	1.3310	1.3328	1.3280	1.3280

[a] [Monomer] = 1.8 mol L^{-1}, [perfluorodibenzoyl peroxide (initiator)] = 0.05 mol L^{-1}, at 41 °C, solvent FC-113.

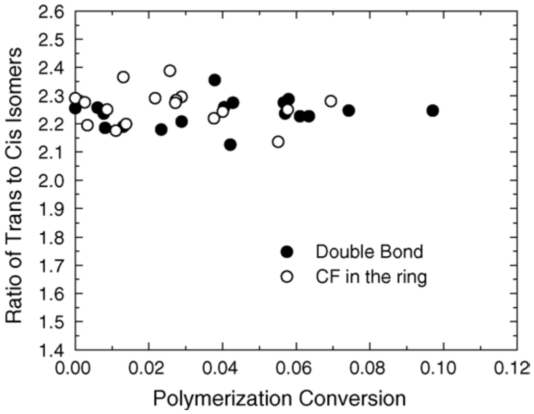


Fig. 6. The dependence of ratio of *trans*- to *cis*-isomers on polymerization conversion for the momomer D.

2-Methylene-1,3-dioxolane monomers with substituents on the 4 position (B and C) were found to be more reactive than those disubstituted monomers (D and E) except monomer A. A decrease in the reactivity of disubstituted monomers may be due to electron withdrawing property of the perfluoro alkyl group substituents and also to the steric hindrance in the polymerization process. However, we could not clarify which factors are dominant. The high reactivity for the monomer A is not clear at present, but may be reduce the steric hindrance by the fused five member ring.

For monomer D, there are *cis*- and *trans*-isomers. The ratio of *cis*- to *trans*-isomers with the polymerization progress was followed by measuring ^{19}F NMR on the vinyl and ring substituted F atoms, and found to be constant. Thus, the reactivity of the *cis*- and *trans*-isomers was same, as shown in Fig. 6.

When these monomers were polymerized in bulk at 60–80 °C for 24–35 h, the conversions were more than 90%. The polymer rods obtained were colorless and transparent. However, when the rods were exposed to air they became hazy. Thus, these polymers were purified by precipitation of their C_6F_6 solutions in chloroform. The purified polymers show no carbonyl groups in IR spectra indicating that the possible ring-opening structures formed in bulk polymerization were removed after purification [8]. The films casted from the C_6F_6 solution of purified polymer were clear and transparent from UV to near IR region even when they were kept in air at room temperature for a long period of time (over 6 months). The polymers have low refractive indexes (Table 1) and also have good thermal stability and their initial decomposition temperatures were higher than 350 °C under nitrogen atmosphere. Their glass transition temperatures were in the region of 100–170 °C (Table 1). The polymers do not show any melting endotherm under 350 °C in their DSC traces. This indicates that these polymers are amorphous. These properties make perfluoro-4,5-substituted-1,3-dioxolane polymers good candidates as optical and electrical materials.

4. Conclusions

A NMR sampling device was designed and constructed to follow the homopolymerizations rate of the perfluoro-2-methylene-1,3-dioxolane derivatives. The NMR sample tube has an insert filled with d_6-DMSO for sample locking. FC-113 or α,α,α-trifluorotoluene solutions of monomers, instead of pure monomers, were utilized to obtain high quality ^{19}F NMR spectra. Using this technique, the monomer concentration as a function of polymerization time could be accurately determined. As a result, it was possible for us to relate polymerization rate with monomer structure and initiator concentration. Poly(perfluoro-4,5-substituted-2-methylene-1,3-dioxolane)s obtained are chemically and thermally stable and transparent from UV to near IR regions. Their glass transition temperatures are 100–170 °C, and they are completely amorphous. Thus, these polymers may be useful materials for opto-electronic devices.

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