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Synthesis and polymerization of a novel perfluorinated monomer

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Abstract

Perfluoro(5-methylene-2,2-dimethyl-1,3-dioxolane) (**1**) was synthesized by utilizing a direct fluorination reaction. Compound **1** was an entirely novel monomer with difluoromethylene at position 5 on the dioxolane ring as an unprecedented polymerization site. It successfully polymerized with tetrafluoroethylene to afford copolymers, which had T_g values in the range of 60–90 °C. The content of monomer **1** in the obtained polymers was less than 20 mol%, which seemed insufficient for giving various unique properties to polymers. However, each polymer was expected to be a superior material because of their advanced thermal stability. Comparison with copolymers of 2,2-bis(trifluoromethyl)-4,5-difluoro-1,3-dioxole and tetrafluoroethylene is also discussed.

Keywords: Perfluorinated monomer; Dioxolane; Fluorination; Thermal stability

1. Introduction

Perfluorinated polymers are known as specialty chemicals for many applications because of their unique properties, e.g. enhanced chemical and thermal stability, or optical and electrical properties [1]. In particular, perfluorodioxolane- or perfluorodioxole-based amorphous polymers, like the copolymers of 2,2-bis(trifluoromethyl)-4,5-difluoro-1,3-dioxole (PDD) and tetrafluoroethylene (TFE) well known as Teflon® AF by DuPont, have received great attention in the development of advanced optical, electrical and chemical materials. Thus, several perfluorinated monomers with a cyclic structure have been synthesized, and polymerization of them has also been reported [1–6]. Although there have been various examples of the synthesis of such monomers, it should be noted that species of polymerization site are still limited, and in many cases compounds with good reactivity have a structure based on only perfluoro(2-difluoromethylene-1,3-dioxolane) or perfluoro(4,5-difluoro-1,3-dioxole).

Recently, our group has developed new and innovative methodology for the synthesis of various perfluorinated compounds via a direct fluorination reaction (Scheme 1) [7–11]. From the perspective of applicability for synthesizing desired perfluorinated compounds, the methodology would be superior to other perfluorination reactions. Substantially, most of the desired fluorine-containing compounds could be obtained by construction of the backbone structure in the hydrocarbon component at will, followed by perfluorination with elemental fluorine. Taking the superiority into consideration, compounds having a novel polymerization site would probably become available and would be candidates for new materials with superior properties.

Herein, we report the synthesis and polymerization with TFE of perfluorinated compound **1**, which has a difluoromethylene structure at position 5 on the dioxolane ring as an unprecedented polymerization site. In addition, the thermal properties of the obtained polymers are also described.

2. Results and discussion

2.1. Synthesis of perfluoro[5-methylene-2,2-dimethyl-1,3-dioxolane]

The perfluorinated monomer **1** (Fig. 1) was successfully synthesized from acyl fluoride **2**, which was obtained by our direct fluorination process, as shown in Scheme 2.

The first step of this synthesis is esterification of 5-hydroxyethyl-2,2-dimethyl-1,3-dioxolane (**6**) with perfluoroacyl

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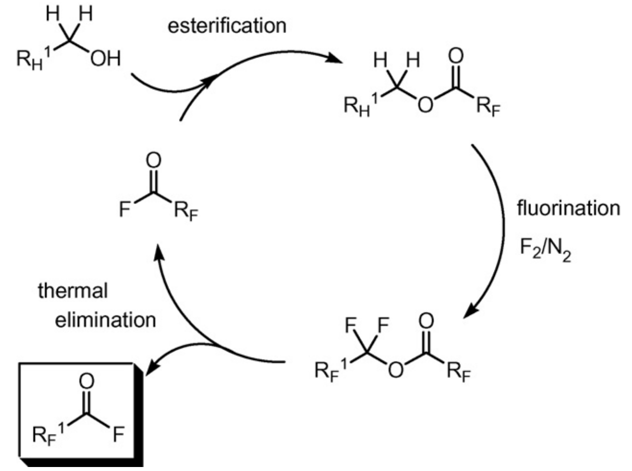

Scheme 1. New methodology for producing desired perfluorinated compounds.

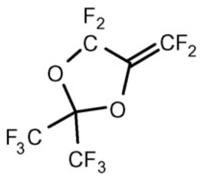

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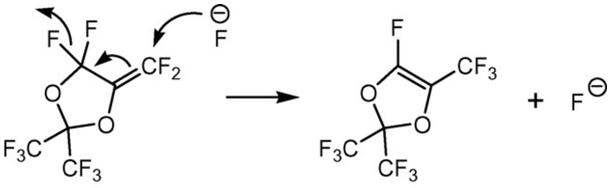
Fig. 1. Compound **1**.

fluoride **5** in the presence of sodium fluoride as an HF scavenger. It was simply carried out by dropwise addition of acyl fluoride **5** to alcohol **6** to give partially fluorinated ester **4** with a good yield. Removal of HF generated during the esterification reaction was essential because of the acid-labile 1,3-dioxolane ring. Shortage of sodium fluoride led to production of undefined complex byproducts that might be caused by ring opening reaction of 1,3-dioxolane.

After distillation, the obtained ester was fluorinated with elemental fluorine diluted with nitrogen in the same manner as described in the literature [7–10]. In the case of using 20 vol% fluorine/nitrogen gas, the yield of the perfluorinated ester **3** determined by ^{19}F NMR was 86%. Though no decomposition was observed, compounds having residual C–H bonds, especially a tertiary one, remained as main byproducts.

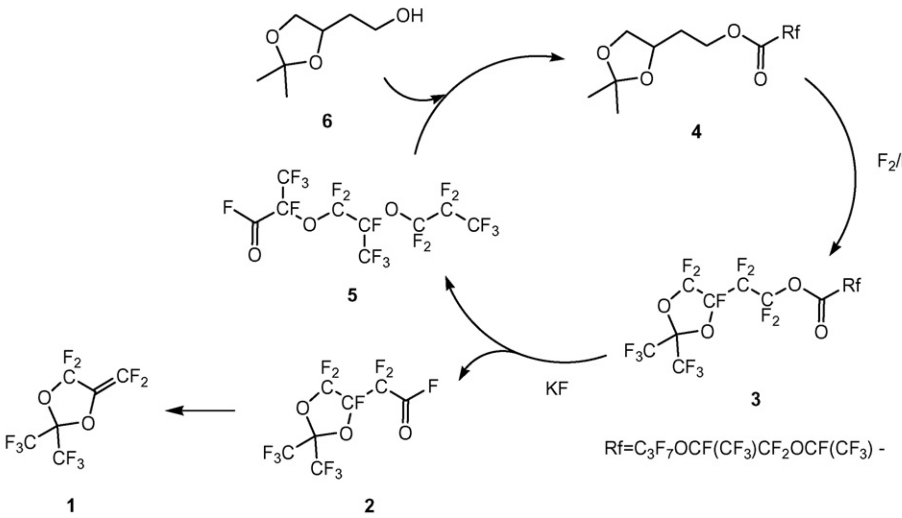


Scheme 3. Isomerization of compound **1** with a fluoride ion.

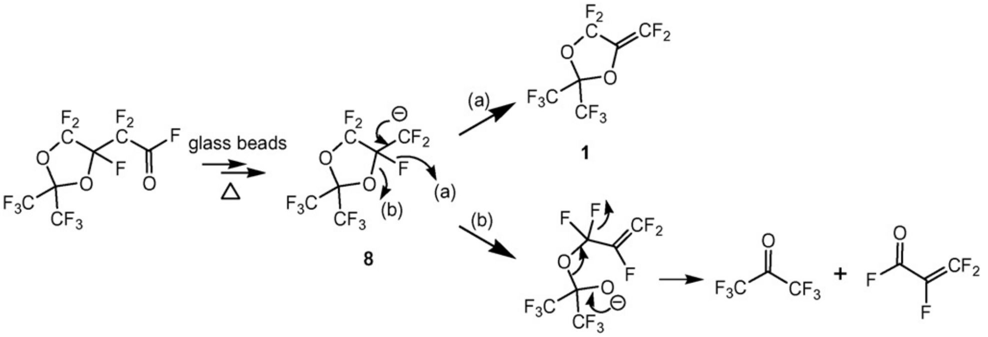
Without any purification, thermal elimination reaction of the ester was carried out with potassium fluoride as a catalyst. A suspension of the ester and KF powder was heated at around 100 °C to give the desired perfluoroacyl fluoride **2** and the starting acyl fluoride **5** by decomposition of the ester bond. Compound **2** was purified by distillation. The separated acyl fluoride **5** could be recycled for the esterification step, as shown in Scheme 2.

Compound **2** was directly converted to the target monomer **1** by pyrolysis. The acyl fluoride **2** was fed on glass beads at over 320 °C, and gas from the outlet of the reactor was condensed in a trap cooled with liquid nitrogen. Analytical data of NMR, GC and GC–MS obviously indicated that compound **1** was the main component in the obtained liquid. It was purified by distillation up to 99% in GC analysis. Peaks assigned to difluoromethylene at position 5 of compound **1** were separately observed at −92.5 and −107.0 ppm in the ^{19}F NMR spectrum. In addition, other peaks corresponding to trifluoromethyl groups and –OCF_2– appeared at −81.4 and −69.3 ppm respectively. The above NMR spectrum data satisfactorily meet to determine the exomethylene cyclic structure of compound **1**.

According to ^{19}F NMR spectrum, one of the byproducts is estimated to be compound **7**, which is an isomer of compound **1**. It was probably produced by isomerization of compound **1** itself with a fluoride ion (Scheme 3). The discriminative peak



Scheme 2. Synthesis of compound **1**.



Scheme 4. Proposed side-reaction during pyrolysis.

Table 1
Results of copolymerization

No.	T [°C]	**1** in feed [mol%]	**1** in polymer [mol%]	Initiator [wt%]	Yield [%]	Mn ×10^4	Mw ×10^4	T_g [°C]	T_d[a] [°C]
1	80	48.8	6.6	0.3[b]	4.4	2.0	2.9	63.8	403.9
2	80	74.0	15.0	0.2[b]	0.7	1.8	2.3	71.8	392.0
3	100	71.6	19.0	0.2[c]	1.2	4.3	6.0	90.0	389.9

[a] Temperature in the case of a weight loss of 10% under nitrogen.

[b] $(C_6F_5COO)_2$.

[c] $(CF_3)_3COOC(CF_3)_3$.

assigned to =CF was observed at −132.6 ppm, and peaks of three trifluoromethyl groups were detected at −66.4 and −82.4 ppm at an integral intensity ratio of 1:2.

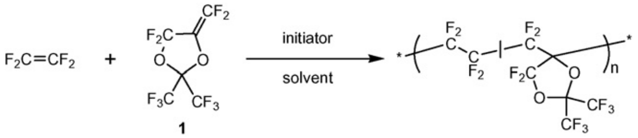
In addition, 2,3,3-trifluoroacryloyl fluoride estimated from the data of ^{19}F NMR and GC–MS was condensed in the cooled trap. Furthermore, hexafluoroacetone (HFA) was also detected when GC analysis of the outlet gas was directly carried out. Thermal decomposition of the dioxolane ring, as illustrated in Scheme 4, might cause their generation. Path (a) illustrated in Scheme 4 leads to formation of the desired compound **1** via elimination of a fluoride ion. However, path (b) results in cleavage of the C–O bond, followed by fragmentation to HFA and 2,3,3-trifluoroacryloyl fluoride. The reaction of the carbanion intermediate **8** can competitively proceed by these two pathways.

Regarding the decomposition of the dioxolane ring, Hung has reported similar phenomena during synthesis of PDD [12]. The estimated cleavage of the C–O bond of dioxolane supports the possibility of Scheme 4, even though the position of the anion of each intermediate was different. In the case of PDD, a rearrangement reaction to an isomeric epoxide was also observed. The somewhat analogous structure of monomer **1** suggests a similar reaction. Although no evidence has been obtained, such a kind of reaction might have occurred.

2.2. *Copolymerization of novel monomer **1** and TFE*

Compound **1** successfully underwent copolymerization with TFE leading to the formation of a novel polymer when initiated by perfluorobenzoyl peroxide (PFBPO) or perfluoro(*tert*-butyl peroxide) (Scheme 5).

Polymers with different contents of monomer **1** from 6% to about 20% were obtained as a white powder (Table 1). The compositions of each polymer was analyzed by molten state NMR. There was a tendency for a higher molecular weight and content of monomer **1** to be obtained in the case of a polymerization at a higher temperature. However, compound **1** unfortunately failed to homopolymerize, in contrast to the case of PDD [1,13,14]. Furthermore, both the yield of polymer and content of monomer **1** in the polymer were not high, which



Scheme 5. Copolymerization of compound **1** and TFE.

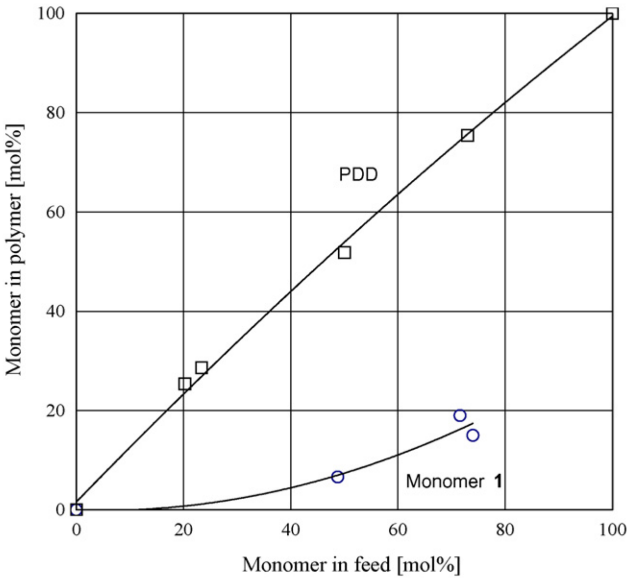
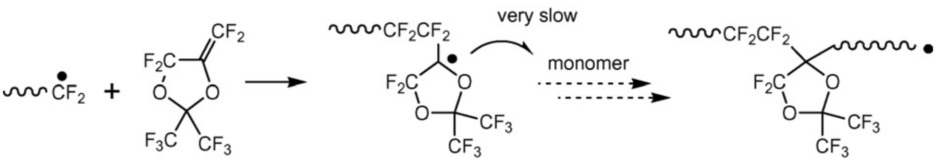
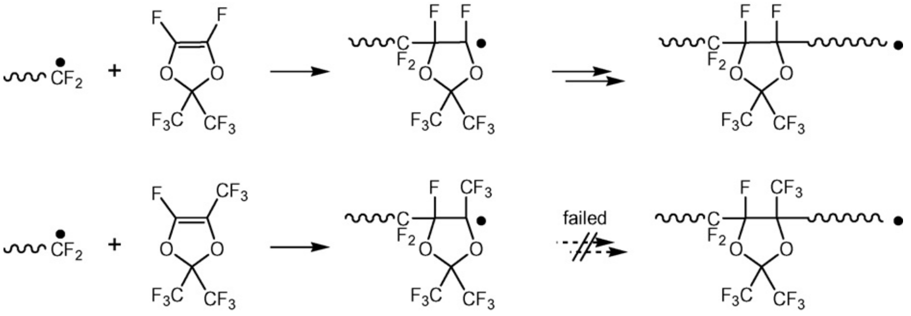


Fig. 2. Copolymerization curve of monomer **1**/TFE (circles) and PDD/TFE (squares) [1,13,14].



Scheme 6. Polymerization reaction of compound **1** and TFE.



Scheme 7. Difference in polymerization reaction between PDD and 2,2,4-tris (trifluoromethyl)-5-fluoro-1,3-dioxole [15].

indicated that compound **1** has relatively low reactivity. The copolymerization curve compared with that of PDD as illustrated in Fig. 2 obviously supported the above result. We estimated that the reactivity might be markedly influenced by a steric effect. When a radical is generated at position 5 during polymerization, the bulky dioxolane ring will prevent the radical from approaching the next monomer (Scheme 6). This conclusion appears reasonable if we consider the difference in polymerization reaction rate between PDD and 2,2,4-tris (trifluoromethyl)-5-fluoro-1,3-dioxole [15]. Hung reported that the failure of copolymerization of the latter monomer with TFE would be due to steric bulkiness (Scheme 7). In contrast, perfluoro-4-methoxy-1,3-dioxole monomer, which has a substitution group at position 4 as well, nevertheless showed a good reactivity [6]. It is expected that the methoxy group could easily rotate around an ethereal oxygen to reduce steric hindrance.

The T_g values of the new copolymers were determined by DSC during second heating at a heating rate of 10 °C/min. They exhibited a clear glass transition and their T_g values were found to be around 60–90 °C. As shown in Fig. 3, introduction of monomer **1** is likely to contribute to an increase of T_g. The increase might be attributable to the fixed and bulky ring structure of the dioxolane unit, giving less conformational flexibility to the polymer. Compared with the copolymer of PDD/TFE with a similar range of monomer content, the T_g value of the obtained copolymer was slightly higher. This might be due to the flexibility of each polymer whose dioxolane rings differently occupy the surrounding space and interact with polymer chains. Currently, a polymer with less than 20 mol% of monomer **1** has only been obtained, but higher molecular content of monomer **1** could still be of great interest in the field of amorphous fluoropolymers.

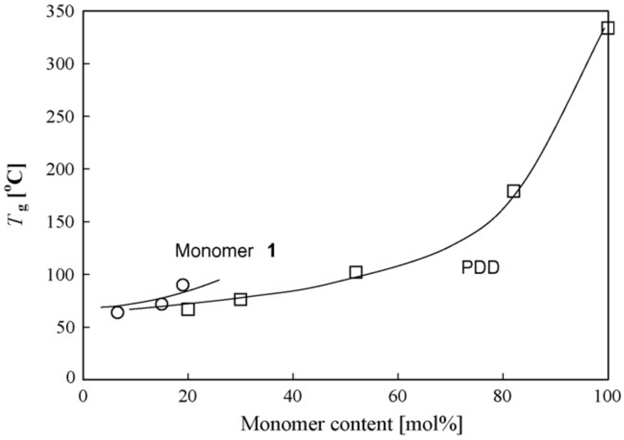


Fig. 3. Dependence of T_g value on each copolymer composition; monomer **1**/TFE (circles) and PDD/TFE (squares) [1,13,14].

A transparent film was successfully obtained by pressing the polymer at 150 °C. However, it was difficult to manage the film and measure the refractive index because of its brittleness, which easily resulted in cracks in the film. In the case of a much higher molecular weight polymer, the film might be more flexible and easier to handle. Regarding thermal stability, on the other hand, these polymers showed good properties, as shown in Table 1. Especially, TGA showed a weight loss of 10% around 400 °C, which is close to that of Teflon® AF [1].

3. Conclusion

In summary, an entirely novel perfluorinated monomer **1** was successfully synthesized by utilizing the direct fluorination process. It copolymerized with TFE to give highly thermally stable copolymers. The obtained copolymers had T_g values of around 60–90 °C, which tended to increase with higher content of monomer **1**. Although monomer content and polymer yield were not high, the new copolymer exhibited superior thermal properties, indicating an open door to valuable potential applications.

4. Experimental

4.1. General

^{1}H NMR (internal TMS) and ^{19}F NMR (internal $CFCl_3$) were obtained with a JEOL AL300 spectrometer. High-resolution mass spectra were obtained with JEOL SX-102A coupled to HP-5890 with a 60 m capillary column J&W DB-1 or DB 1301. DSC was obtained with a TA Instruments DSC Q100. TGA was obtained with a TA Instruments TGA Q500. Elemental fluorine is a highly toxic and corrosive gas, which may cause explosion when it meets organic compounds in the vapor phases, so extreme care must be taken when handling it. Both the liquid and vapor of hydrogen fluoride (bp 19.5 °C) evolved during the reaction are also highly corrosive and cause severe contact burns, so care must be taken! Prior to use, all hydrocarbon grease must be removed and the apparatus must be gradually passivated with elemental fluorine. Although the use of 1,1,2-trichrolotrifluoroethane (R113) is regulated, we have given experimental examples with it for convenience, because it is still much more cheaply available than compound **5** for use as a solvent. Care must be taken to avoid its emission to the environment. Compound **6** was purchased from Daicel Chemical Industries, Ltd. (Japan). Other commercially available materials were used without purification.

4.2. Synthesis of perfluoro (5-methylene-2,2-dimethyl-1,3-dioxiolane) (1)

To a stirred mixture of 103.2 g (0.705 mol) of 5-hydroxyethyl-2,2-demethyl-1,3-dioxolane (**6**) and 59.3 g (1.411 mol) of sodium fluoride in 1600 g of R-225 (mixture of $CF_3CF_2CHCl_2$ and $CClF_2CF_2CHClF$) at 0–5 °C was added dropwise a solution of 421.7 g (0.846 mol) of acyl fluoride **5** over a period of 3 h. After completion of addition, stirring was continued at room temperature for 20 h. The crude mixture was filtered, and the liquid was washed once with saturated $NaHCO_3$ aqueous solution and twice with water, followed by drying over magnesium sulfate. After filtration, the liquid was purified by distillation *in vacuo* (83 °C/1.06 kPa), and ester **4** was obtained (294.5 g, 0.471 mol, 67% yield). The GC purity was 97%.

Compound **4**: ^{1}H NMR (300.4 MHz, $CDCl_3$): δ 1.34 (s, 3H, *m* or *n*), 1.41 (s, 3H, *m* or *n*), 1.97 (dt, ^{3}J = 6.6 Hz, 6.9 Hz, 2H, *j*), 3.59 (dd, ^{3}J = 6.6 Hz, ^{2}J = 7.8 Hz, 1H of *l*), 4.09 (dd, ^{3}J = 6.0 Hz, ^{2}J = 7.8 Hz, 1H of *l*), 4.17 (m, 1H, *k*), 4.53 (m, 2H, *i*); ^{19}F NMR (282.7 MHz, $CDCl_3$): δ −79.0 to −80.5 (1F of *c* and 3F of *e*), −81.8 to −82.7 (8F, *a*, *f* and *h*), −84.5 to −85.5 (1F of *c*), −130.1 (2F, *b*), −132.0 (1F, *g*), −145.6 (1F, *d*) (Fig. 4).

Into a 3000 ml autoclave made of nickel, R113 (1700 g) was charged and stirred at 25 °C. At the outlet of the autoclave, a packed layer of sodium fluoride pellets and a cooler maintained at −10 °C were installed in series. Further, a liquid-returning line was installed to return any condensed liquid from the cooler to the autoclave. After supplying nitrogen gas for 1 h, 20 vol% F_2/N_2 was fed for more 1 h at a flow rate of 16.7 L/h. While feeding 20 vol% fluorine gas at the same flow rate, a solution of compound **4** (72.0 g, 0.115 mol) in R113 (720 g) was introduced over a period of 20.6 h. After the introduction of all the solution, 20 vol% fluorine gas was supplied at the same flow rate for 1 h. Then, nitrogen gas was fed for 2 h to remove fluorine gas and volatile compounds from the autoclave to give a solution of the crude perfluorinated product. The structure of the obtained compound **3** was determined by ^{19}F NMR (93% yield).

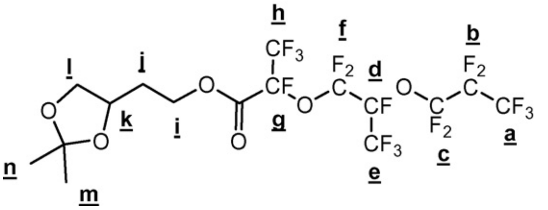


Fig. 4. Compound **4**.

Compound **3**: ^{19}F NMR (282.7 MHz, $CDCl_3$): δ −76.4 to −76.9 (1F of *l*), −79.1 to −81.6 (2F of *c* and *l*, 3F of *e*, *m* and *n*), −82.0 to −82.3 (8F, *a*, *f* and *h*), −84.1 to −85.1 (1F of *c*), −85.6 to −87.5 (2F, *i*), −120.1 (1F, *k*), −122.2 to −123.3 (1F of *j*), −128.1 to −129.7 (1F of *j*), −130.2 (2F, *b*), −132.2 (1F, *g*), −145.5 (1F, *d*) (Fig. 5).

After evaporation of solvent and volatile compounds, crude perfluorinated ester **3** (93.0 g, 0.108 mol) was charged into a flask with 0.93 g (0.016 mol) of potassium fluoride powder. The dispersion was heated at 110 °C and vigorously stirred for 4 h in an oil bath with a reflux condenser at the top of the flask. Distillation of the crude solution provided compound **2** (82 °C/101.3 kPa, 54% yield) and starting acyl fluoride **5**. The structure of compound **2** was confirmed by ^{19}F NMR and GC–MS.

Compound **2**: ^{19}F NMR (282.7 MHz, $CDCl_3$): δ + 24.1 (1F of *i*), −76.6 to −77.1 (1F of *l*), −80.6 to −81.2 (1F of *l*, 6F of *m* and *n*), −115.7 to −116.8 (1F of *j*), −118.2 (1F, *k*), −118.5 to −119.6 (1F of *j*); High-resolution mass spectrum (EI^{+}) 290.9712 ($[M-CF_3]^{+}$, calculated for $C_6F_9O_3$: 290.9704) (Fig. 6).

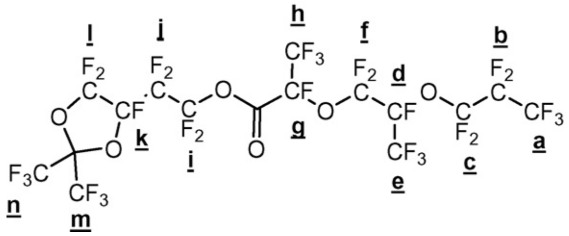


Fig. 5. Compound **3**.

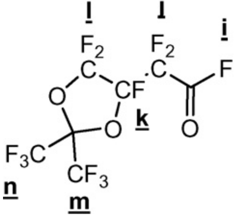


Fig. 6. Compound **2**.

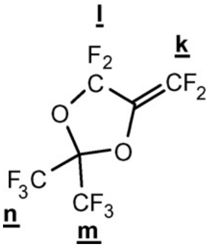


Fig. 7. Compound **1**.

Compound **2** (19.0 g, 0.053 mol) was gradually fed on glass beads maintained at 320 °C using a syringe pump at a feed rate of 9.7 mL/h. Nitrogen gas was introduced into an inlet of the reactor at a flow rate of 5.0 L/h. The gas from an outlet of the reactor was condensed into a trap cooled by liquid nitrogen. The obtained crude liquid was purified by distillation to give 5.7 g (0.019 mol, 37% yield) of the desired monomer **1** with GC purity of 99% (57 °C/101.3 kPa). HFA and 2,3,3-trifluoroacryloyl fluoride were also detected by NMR and GC as side products. Their yields were not determined.

Compound **1**: ^{19}F NMR (282.7 MHz, $CDCl_3$): δ −69.3 (2F, *l*), −81.4 (6F, *m* and *n*), −92.5 (1F of *k*), −107.0 (1F of *k*); high-resolution mass spectrum (EI^+) 293.9690 ($[M]^+$, calculated for $C_6F_{10}O_2$: 293.9739) (Fig. 7).

4.3. Copolymerization of compound 1 and TFE

Compound **1**, CF_2ClCF_2CHClF as a solvent and an initiator (PFBPO or $(CF_3)_3COOC(CF_3)_3$) at 0.2–0.3 wt% were charged into an autoclave. The autoclave was cooled by liquid nitrogen, followed by evacuation and warming to room temperature. The freezing and warming procedure was repeated twice to substantially degas the reactor. After the degassing operation, TFE gas was introduced into the reactor at 80 °C and the mixture was stirred for 5 h, maintaining the temperature. Unreacted TFE gas was purged, and into the crude solution was poured CH_3CCl_2F to precipitate a produced polymer. Filtrated polymer was dried at 80 °C *in vacuo* to give a white powder. Monomer content of the obtained polymers was determined by molten state NMR. The temperature of the glass transition point and the temperature of weight loss of 10% were determined by DSC and TGA, respectively.

References

[1] P.R. Resnick, W.H. Buck, in: J. Schirs (Ed.), Modern Fluoropolymers, John Wiley and Sons, 1997.
[2] S. Selman, E.N. Squire, US Patent 3,308,107 (1967).
[3] References are cited therein
(a) Y. Yang, F. Mikes, L. Yang, W. Liu, Y. Koike, Y. Okamoto, J. Fluorine. Chem. 127 (2006) 277–281;
(b) Y. Yang, F. Mikes, L. Yang, W. Liu, Y. Koike, Y. Okamoto, J. Polym. Sci., Part A: Polym. Chem. 44 (2006) 1613–1618.
[4] N. Sugiyama, WO2005085303 (2005).
[5] T. Okazoe, A. Watakabe, M. Ito, K. Watanabe, T. Kashiwagi, S.-Z. Wang, WO2003037885 (2003).
[6] References are cited therein
(a) A. Russo, W. Navarrini, J. Fluorine Chem. 125 (2004) 73–78;
(b) W. Navarrini, V. Tortelli, A. Russo, S. Corti, J. Fluorine Chem. 95 (1999) 27–39.
[7] T. Okazoe, K. Watanabe, M. Itoh, D. Shirakawa, H. Murofushi, S. Tatematsu, Adv. Synth. Catal. 343 (2001) 215–219.
[8] T. Okazoe, K. Watanabe, M. Itoh, D. Shirakawa, S. Tatematsu, J. Fluorine Chem. 112 (2001) 109–116.
[9] T. Okazoe, E. Murotani, K. Watanabe, M. Itoh, D. Shirakawa, K. Kawahara, I. Kaneko, S. Tatematsu, J. Fluorine Chem. 125 (2004) 1695–1701.
[10] T. Okazoe, K. Watanabe, M. Itoh, D. Shirakawa, K. Kawahara, S. Tatematsu, J. Fluorine Chem. 126 (2005) 521–527.
[11] G. Standford, J. Fluorine Chem. 128 (2007) 90–104.
[12] M.-H. Hung, W.B. Farnham, J. Chin. Chem. Soc. 40 (1993) 563–569.
[13] C.D. Wood, U. Michel, J.P. Rolland, J.M. DeSimone, J. Fluorine Chem. 125 (2004) 1671–1676.
[14] U. Michel, P. Resnick, B. Kipp, J.M. DeSimone, Macromolecules 36 (2003) 7107–7113.
[15] M.-H. Hung, Macromolecules 26 (1993) 5829–5834.