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Novel Fluorinated Dioxolane Oxazoline Polymers[1-3]

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Introduction

Fluoropolymers have a unique combination of properties. They exhibit excellent thermal stability, high chemical resistance, and very low surface energy, unmatched by other polymers.[4] Rapidly advancing new technologies have resulted in increased needs for fluoropolymers. Poly(tetrafluoroethylene) (PTFE) is the most widely used fluoropolymer, but its processability is hindered by its high crystallinity. Less crystalline copolymers of tetrafluoroethylene with other monomers were developed which are melt processable. Recently, amorphous fluoropolymers have been introduced. These new polymers contain ring structures[5,6] in the main chain and offer enhanced processability.

The unusual structure and properties of oxazoline polymer have also recently attracted much attention,[7] and many applications of polyoxazolines, such as gelling[8] and antistatic agents,[9] have been developed. Oxazoline polymers are also useful as nonionic surfactant[10] and surface modifier.[11] Polyoxazolines are known to be miscible with many commodity polymers[12,13] and are used as compatibilizers to promote adhesion between incompatible materials such as cellulose and poly(vinyl chloride).[14]

In this paper, we describe the synthesis of novel amorphous fluorinated oxazoline monomers and polymers. The improved solubilities of the polymers are demonstrated to be useful for modifying nylon surfaces.

Experimental Section

(I) Preparation of 2,2-Bis(trifluoromethyl)-4-(2-oxazolinyl)-1,3-dioxolane (1). (i) Preparation of 2,2-Bis(trifluoromethyl)-1,3-dioxolan-4-oyl Chloride (1A). Compound 1A was prepared from 2,2-bis(trifluoromethyl)-4-carboxyl-1,3-dioxolane.[15] To this substrate (25.5 g, 0.1 mol) in a round-bottomed flask was added pyridine (3.16 g, 0.04 mol), followed by thionyl chloride (14.3 g, 0.12 mol). External cooling was applied to maintain the pot temperature at 20–25 °C. After the addition was complete, the reaction mixture was warmed slowly to 70 °C in 1.5 h and then kept at 90–100 °C for 0.5 h. The product was distilled from the reaction mixture as a clear colorless liquid 1A (22.0 g, 81% yield). Bp: 50 °C (10 mm). ^1H NMR (neat) δ 5.23 (t, *J* = 7.0 Hz, 1H, $-OC\mathit{H}CH_2-$), 4.73 (m, 2H). ^{19}F NMR (neat): δ −80.5 (q, *J* = 8.5 Hz, 3F), −81.5 (q, *J* = 8.5 Hz, 3F). Anal. Calcd for $C_6H_3ClF_6O_3$: C, 26.44; H, 1.11; F, 41.83; Cl, 13.00. Found: C, 26.13; H, 1.11; F, 41.44; Cl, 13.38.

(ii) Reaction of 1A with Ethanolamine. 1A (50.57 g, 0.186 mol) was added dropwise to a mixture of ethanolamine (18.56 g, 0.183 mol) and anhydrous dichloromethane (200 mL) at −5 °C with stirring under nitrogen. The reaction was allowed to proceed overnight. The product mixture was washed three times with a saturated NaCl solution (150 mL) and dried over anhydrous sodium sulfate. A brown paste (51.54 g) was obtained after removal of the solvent. The target compound (**1B**) was obtained after distillation at the boiling point 111.2–111.5 °C (0.1 mm) (yield 19.4 g). The structure of compound **1B** was characterized by ^1H NMR and IR. ^1H NMR ($CDCl_3$, TMS): δ 2.72 (s, br, 1H, OH), 3.50 (m, 2H, NCH_2CO), 3.75 (m, 2H, $NCCH_2O$), 4.34 (t, *J* = 7.9 Hz, 1H, $-OC\mathit{H}_aH_bCHO$), 4.70 (t, *J* = 7.9 Hz, 1H, $-OCH_aC\mathit{H}_bCHO$), 4.95 (t, *J* = 7.7 Hz, 1H, $OC\mathit{H}CH_2O$), 6.89 (s, br, 1H, −NH). IR (neat, cm^{-1}): 3400 (−OH), 1680 (C(=O)NH).

(iii) Preparation of 1C. Thionyl chloride (15.21 g, 0.128 mol) was added dropwise to **1B** (19.0 g, 0.064 mol) in dichloromethane (50 mL) at −5 to 5 °C with stirring under nitrogen. The reaction was carried out for 2 h at 5 °C and then was gradually warmed to ambient temperature. After removal of dichloromethane, **1C** was isolated by distillation [bp 83.2 °C (0.8 mm), 65.9% yield]. ^1H NMR ($CDCl_3$, TMS): δ 3.64 (m, 4H, NCH_2CH_2Cl), 4.34 (t, *J* = 8.1 Hz, 1H, $-OC\mathit{H}_aH_bCHO$), 4.71 (t, *J* = 8.0 Hz, 1H, $-OCH_aC\mathit{H}_bCHO$), 4.95 (t, *J* = 7.7 Hz, 1H, $-OCH_2C\mathit{H}O$), 6.89 (s, br, 1H, −NH). IR (neat, cm^{-1}): 1690 (C(=O)NH).

(iv) Cyclization of 1C. Compound **1C** (9.28 g, 29.44 mmol) was dissolved in methanol (20 mL), and sodium hydroxide pellets (1.73 g, 43.3 mmol) were added. The reaction mixture was stirred at room temperature for 2 h. After removing the MeOH, dichloromethane (30 mL) and a saturated NaCl solution (20 mL) were added to extract the product; the procedure was repeated twice. The organic portions obtained were combined and dried over sodium sulfate. After evaporating the solvent, the desired oxazoline 1 was obtained as a yellow liquid. The compound was purified by vacuum distillation [bp 61 °C (0.25 mm)]. The yield was 7.45 g (71.0%). ^1H NMR ($CDCl_3$, TMS): δ 3.94 (t, *J* = 9.7 hz, 2H, NCH_2), 4.40 (t, *J* = 9.2 Hz, 2H, OCH_2), 4.50 (t, *J* = 7.9 Hz, 1H, $-OC\mathit{H}_aH_bCHO$), 4.57 (t, *J* = 7.3 Hz, 1H, $-OCH_aC\mathit{H}_bCHO$), 5.07 (t, 7.2 Hz, 1H, $-OCH_2C\mathit{H}O$). ^{19}F NMR (neat): δ −80.5 (m, 3F), −81.0 (m, 3F). IR (neat, cm^{-1}): 1680 (OC=N−). Anal. Calcd for $C_8H_7F_6NO_3$: C, 34.30; H, 2.52; F, 40.36; N, 4.99. Found: C, 34.42; H, 2.53; F, 40.84; N, 5.02.

(II) Synthesis of 2-(4-Perfluoro-2,2-dimethyl-1,3-dioxolanyl)ethyl-2-oxazoline (2). (i) Preparation of 2B. In a pressure vessel was charged perfluoro-2,2-dimethyl-1,3-dioxole (**2A**;[2c] 48.8 g, 0.2 mol), mercury(II) oxide (yellow form, 45 g, 0.208 mol), iodine (127 g, 0.5 mol), phenothiazine (0.1 g), and hydroquinone (0055 g). The tube was cooled and evacuated, and hydrogen fluoride (12 g, 0.6 mol) was transferred into the tube. The tube was sealed and was heated at 50 °C for 2 h. The temperature was then raised from 50 to 125 °C in 2 h and was kept at 125 °C for another 3 h. The product mixture was carefully dumped into ice water, and the bottom organic layer was separated. The desired 2,2-bis(trifluoromethyl)-4-iodo-4,5,5-trifluoro-1,3-dioxolane (**2B**) was purified by distillation [yield 50 g (64%)]. This product is a clear, colorless liquid (bp 74–76 °C). ^{19}F NMR (neat): −46.6 (m, br, 1F), −87.7 (dm, *J* = 129 Hz, 1F), −80.9 (s, br, 6F).

(ii) Preparation of 2C. 2B (11.7 g, 0.03 mol) was mixed with ethylene (5 g, 0.179 mol) in a 75-mL pressure vessel. The tube was sealed and heated at 220 °C for 10 h. The product mixture was distilled to afford 2,2-bis(trifluoromethyl)-4-(2-iodoethyl)-4,5,5-trifluoro-1,3-dioxolane (**2C**) as a light pink liquid with a boiling point of 95 °C (100 mm). ^1H NMR (neat): δ 2.0 (m, 2H), 3.43 (m, 2H). ^{19}F NMR (neat): δ −110.0 (m, 1F), −77.8 (dm, *J* = 137.5 Hz, 1F), −88.3 (dd, *J* = 137.5 Hz, 8.5 Hz, 1F), −80.9 (m, 3F), −81.6 (m, 3F).

(iii) Dehydroiodination of 2C. 2C (16.72 g, 0.04 mol) was mixed with 10 M KOH (20 mL, 0.20 mol) and bis(2-hydroxypropyl)benzyldodecylammonium chloride phase-transfer catalyst (60% w/w aqueous solution, 0.855 g, 0.002 mol) and was vigorously stirred at room temperature. The reaction was monitored by gas chromatography and was stopped when the conversion of the starting material was complete. The bottom organic layer was separated, washed with water and dilute HCl, and then distilled to afford 2,2-bis(trifluoromethyl)-4-vinyl-4,5,5-*trifluoro-1,3-dioxolane* (**2D**; *9.5 g, 82% yield*) as a clear, colorless liquid (bp 70–72 °C). ^1H NMR (neat): δ 5.40–5.90 (m). ^{19}F NMR (neat): δ −112.8 (m, 1F), −75.7 (dm, *J* = 140 Hz, 1F), −90.3 (dd, *J* = 140, 10.5 Hz, 1F), −82.0 (m, 3F), −82.6 (m, 3F).

(iv) Hydrocyanation of 2D. A mixture comprised of $Ni[P(\mathit{O}\text{-tolyl})_3]_4$ (3.3 g, 2.2 mmol), $P(\mathit{O}\text{-tolyl})_3$ (1.7 g, 4.8 mmol), **2D** (30 g, 0.103 mol), 25% $EtAlCl_2$ in toluene (2.0 mL), and toluene (25 mL) was heated under nitrogen in an oil bath at 60 °C. A 50% solution of HCN in toluene was fed from an ISCO pump at a rate of 1.5 mL/h for 4.5 h and then 0.5 mL/h overnight until the reaction was complete (gas chromatography determination). The mixture was allowed to cool and was purified by distillation to give 2,2-bis(trifluoromethyl)-4-(2-cyanoethyl)-4,5,5-trifluoro-1,3-dioxolane (**2E**) as a clear, colorless liquid in 66% yield. Bp: 65–

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68 °C (7.0 mm). ^{1}H NMR (CDCl$_3$): δ 2.72 (t, J = 7.8 Hz, 2H), 2.50 (m, 2H). ^{19}F NMR (CDCl$_3$): δ −110.2 (m, 1F), −76.9, −77.6 (2m, 1F), −87.0, −87.7 (2d, J = 9.3 Hz, 1F), −80.6 (m, 3F), −81.3 (m, 3F). Anal. Calcd for $C_8H_4F_9NO_2$: C, 30.28; H, 1.27; F, 53.94. Found: C, 30.21; H, 1.34; F, 54.26. MS [M]. Calcd: 317.0098. Found: 317.0081. MS(PCI) [M + H]. Calcd: 318.0177. Found: 318.0176.

(v) Reaction of 2E with Ethanolamine. **2E** (10 g, 31.55 mmol), ethanolamine (1.93 g), and $Cd(OAc)_2{\cdot}2H_2O$ (0.421 g, 1.58 mmol) were added to a round-bottomed flask with stirring. The reaction mixture was heated at 130 °C for 20 h. All the material that distilled under vacuum (20 mmHg) at 100 °C was collected and purified by redistillation. The 2-(4-perfluoro-2,2-dimethyl-1,3-dioxolanyl)ethyl-2-oxazoline (**2**) was obtained at 94.7–95.7 °C (25 mmHg). The yield was 7.36 g (64.6%). ^{1}H NMR (CDCl$_3$, TMS): δ 2.41–2.60 (m, 4H), 3.85 (t, J = 9.5 Hz, 2H), 4.28 (t, J = 9.5 Hz, 2H). IR (neat): 1700 cm^{-1} (−N=CO), absence of 2350 cm^{-1}. Anal. Calcd for $C_{10}H_8F_9NO_3$: C, 33.22; H, 2.12; F, 47.42; N, 3.89. Found: C, 33.26; H, 2.23; F, 47.34; N, 3.88.

(III) Polymerization. (i) Polymerization of 1. Oxazoline **1** (0.63 g, 2.26 mmol) was first charged into a 25-mL predried ampule under nitrogen, and methyl p-toluenesulfonate (MeOTs; 0.0167 g) was introduced by microsyringe with vigorous stirring. The ampule was then sealed and kept in a 90 °C oil bath for 24 h. The reaction mixture solidified during polymerization. Chloroform (20 mL) was added to dissolve the solid, and then a small amount of n-butylamine (1–2 mL) was added to quench the polymer reaction. The mixture was poured into hexane (100 mL) to precipitate the polymeric material. Due to the high solubility of the polymer, a large amount of polymer was recovered from supernatant. After workup, 0.14 g of polymer was obtained from the precipitate and 0.47 g of polymer was recovered from the supernatant. The total yield of polymer **3** is 93.4%. The structure of polymer **3** was characterized by proton NMR, IR, and gel permeation chromatography (GPC) (HFIP eluent with PET standard). Both the precipitate and polymer recovered from supernatant were combined for GPC measurement. ^{1}H NMR (CDCl$_3$ with TMS): δ 3.53 (s, br, NCH$_2$CH$_2$–, 4H), 4.30 (s, br, OCH_aH$_b$CHO, 1H), 4.65 (s, br, −OCH$_a$CH_bCHO), 4.81 (s, br, 1H, −OCH$_2$CHO). IR (neat): 1670 cm^{-1} (−NC=O).

(ii) Polymerization of 2. Oxazoline monomer **2** (0.58 g, 1.6 mmol) was charged into a predried 20-mL ampule by syringe. Then MeOTs (0.015 g, 0.08 mmol) was added dropwise with stirring under nitrogen. The mixture was cooled in ice–water, and the ampule was sealed. After heating the ampule at 90 °C for 24 h (the solution solidified within 2 h), hexafluoroisopropyl alcohol (HFIP; 10 mL) was added to dissolve the reaction mixture. Then n-butylamine (1 mL) was added to quench the polymerization reaction. The product mixture was poured slowly into hexane (100 mL) to precipitate polymeric material. White powdered polymer **4** (0.52 g, 87.7%) was isolated after filtration; another 0.06 g (10.1%) of polymer was recovered from the supernatant. ^{1}H NMR (CDCl$_3$, TMS): δ 2.3–2.7 (s, br, 4H, C(O)CH$_2$CH$_2$), 3.5 (s, br, 4H, NCH$_2$CH$_2$). IR (neat): 1650 cm^{-1} (−NC=O). Anal. Calcd for $C_{10}H_8F_9NO_3$: C, 33.22; H, 2.12; F, 47.42; N, 3.89. Found: C, 33.12; H, 2.29; F, 47.25; N, 3.73.

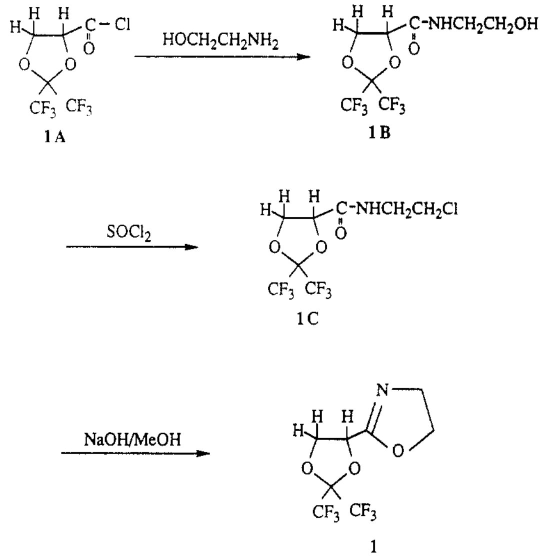
Results and Discussion

The oxazoline monomer **1**, which has no spacer group between fluorinated dioxolane and oxazoline rings, was synthesized by the condensation of acyl chloride **1A** with ethanolamine, followed by the chlorination of **1B**, and intramolecular cyclization of **1C** as shown in Scheme I.

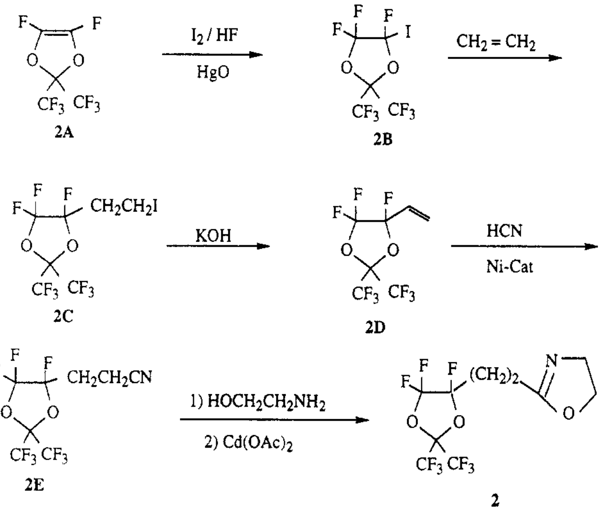
Monomer **2**, which has two methylene spacer groups between the rings, was prepared by reaction of nitrile **2E** with ethanolamine in the presence of a cadmium catalyst according to Witte.[16] Compound **2E** was prepared according to the Scheme II from perfluoro-2,2-dimethyl-1,3-dioxole.

Both monomers were successfully ring-opening polymerized by cationic initiator MeOTs to form the amide polymers **3** and **4** (Scheme III). The polymerization results are summarized in Tables I and II.

Scheme I



Scheme II



Scheme III

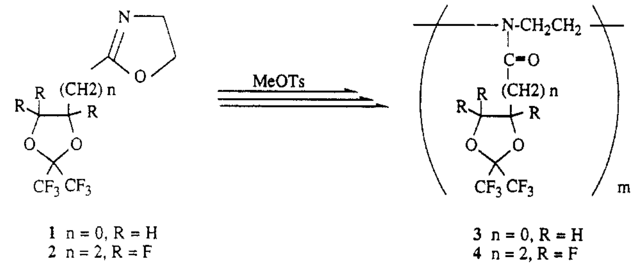


Table I. Polymerization of Oxazoline 1

no.[a]	1 (mmol)	MeOTs (mmol)	solvent	yield[c] (%)	M_w[e]	MWD[e]
1	2.26	0.090		94.3	17700	3.13
2	1.98	0.087	DMF	89.1	8830	5.04
3	1.69	0.068[b]		100	14500	7.41
4	2.03	0.012		91.5	7220	3.29
5	2.12	0.086	CHCl$_3$	41.2[d]	6190	4.21

[a] Polymerized at 90 °C for 48 h. [b] $BF_3{\cdot}OEt_2$ was used as initiator. [c] Total yields of precipitant and dry residue of supernatant from hexane solution. [d] The yield of precipitant. [e] Measured by GPC in HFIP with PET as standard.

The polymers were isolated by precipitating the polymerization reaction mixture into a large amount of hexane. The polymers obtained are readily dissolved in common solvents such as N,N-dimethylformamide (DMF)

Table II. Polymerization of Oxazoline 2

no.[a]	2 (mmol)	MeOTs (mmol)	solvent	yield[b] (%)	M_w[c]	MWD[c]
1	1.60	0.080		87.7	5190	1.16
2	1.49	0.064	$CHCl_3$	43.2	4650	1.10
3	1.62	0.004		95.6	5730	1.13
4	2.01	0.005	$CHCl_3$	75.6	4490	1.05

[a] Polymerized at 90 °C for 24 h. [b] Precipitated in hexane. [c] Measured by GPC in THF with PS as standard.

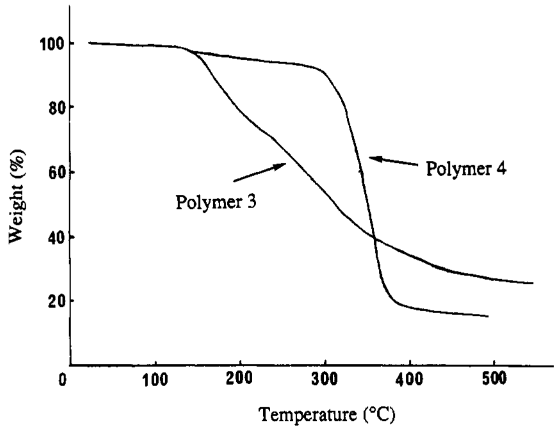


Figure 1. TGA of polymers 3 and 4 (heating rate 10 °C/min under a N_2 purge).

and chloroform ($CHCl_3$).

The polymerization mechanism of 1 was rather complicated, and the molecular weight distribution measured from GPC was not monodispersed. Steric congestion from the dioxolane and oxazoline ring structures presumably plays an important role. On the other hand, the polymerization of 2 with MeOTs initiator is believed to proceed via an oxazolinium tosylate, like other 2-alkyl-2-oxazolines,[7] as judging from the narrow molecular weight distribution of the resulting polymers.

Clear glass transition temperatures for polymers 3 and 4 were observed at 7.8 and 30.1 °C, respectively, by differential scanning calorimetry measurements. These results confirm the amorphous characters of these polymers. The thermal stabilities of 3 and 4 were quite different from thermogravimetric analysis (TGA). The onset of decomposition of 3 was observed at about 130 °C, but polymer 4 only started to decompose at about 300 °C as shown in Figure 1. It is quite likely that both the stronger electron-withdrawing nature of the fluorinated dioxolane ring and the sterically hindered structure in polymer 3 are related to the weaker thermal stability of 3. In polymer 4, the ethylene spacer group between the main chain and the dioxolane group may improve the stability, bringing it closer to those of alkyloxazoline polymers.

By coating a chloroform solution of polymer 4 (10 wt %) on a 6,6-Nylon film surface, the water contact angle of the nylon film increased from 57 to 95°. Due to the highly polar chain structure of 4, it should exhibit excellent compatibility with nylon,[11] and the coating is expected to last for a considerable length of time. In a separate experiment, blends of up to 10 wt % of 4 with nylon were prepared in a HFIP solvent and no change was observed in the contact angle of a casted film surface. In the latter case, it may be that the miscibility of nylon and 4 is too good so polymer 4 would not migrate to the blended film surface. This result is contradictory to our observations on blends of nylon with oxazoline polymers that have long perfluoroalkyl chains.[11]

Summary

We have synthesized a novel class of fluorinated polyoxazolines, combining the characteristics of fluorodioxolane and oxazoline polymers. These new polymers are amorphous and readily dissolve in most common organic solvents, such as DMF and $CHCl_3$. By a simple coating technique, these polymers were found to be useful in surface modification of the polar hydrocarbon polymers.

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