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SYNTHESIS AND POLYMERIZATION OF ETHYNYLTHIOPHENES AND ETHYNYLFURANS CONTAINING TRIFLUOROMETHYL GROUPS

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SUMMARY

Fluorination of thiophenedicarboxylic acid with sulfur tetrafluoride in the presence of anhydrous hydrogen fluoride provided mono and bis(trifluoromethyl)thiophenes in moderate yields. Ethynylthiophenes and ethynylfurans containing trifluoromethyl groups were prepared via 2,2-dichloro-1-fluorovinyl compounds. In polymerizations using transition metal catalysts, 3-ethynylthiophenes gave polymers in high yields, which were soluble in THF and/or fluorocompounds, while 2-ethynylthiophenes polymerized in low yields. In γ-ray induced polymerization, only 2,5-bis(trifluoromethyl)-3-ethynylthiophene afforded the corresponding polymers. Thermal decomposition temperatures of polymers obtained increased by introduction of the trifluoromethyl groups as well as the methyl groups.

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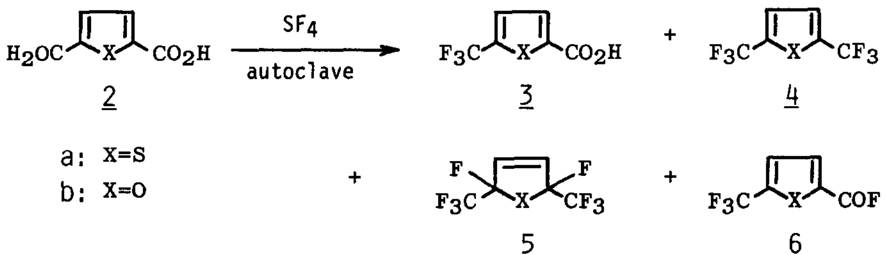
INTRODUCTION

Polymers containing highly conjugated systems, such as polyacetylenes and poly(thiophenediyl)s, are of interest as possible organic conductors and chromatic materials. Recently both poly(2-ethynylthiophene) and poly(3-ethynylthiophene) proved to work as semiconductors by I_2-doping [1, 2]. We have evaluated polymerization of CF_3-substituted phenylacetylenes and properties of the polymers obtained [3 - 5]. We also synthesized some 2-ethynyl(trifluoromethyl)furans, but they produced insoluble polymers by thermal polymerization and low molecular weight oligomers by γ-ray induced polymerization [6]. The present work deals with synthesis and polymerization of ethynylthiophenes and ethynylfurans having trifluoromethyl groups, and with trifluoromethyl substituent effects on polymerization and polymer properties.

RESULTS AND DISCUSSION

Introduction of trifluoromethyl groups into thiophene

Fluorination of a carboxylic group with sulfur tetrafluoride is a useful method for introduction of the trifluoromethyl group into aromatic rings [7]. The fluorination of 2,5-furandicarboxylic acid (2b) with sulfur tetrafluoride provides 2,5-bis(trifluoromethyl)furan (4b), but in the presence of anhydrous HF, 4b is readily converted into 2,5-difluoro-2,5-bis(trifluoromethyl)-2,5-dihydrofuran (5b) by the addition of fluorine atoms to the ring [8, 9]. We achieved the reaction of 2,5-thiophene- and -furan-dicarboxylic acid (2) with sulfur tetrafluoride and anhydrous HF (Scheme 1).



Scheme 1

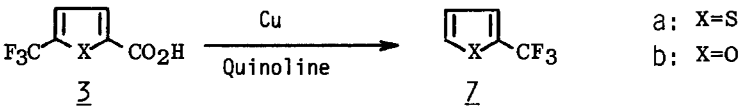
TABLE I

Fluorination of 2,5-Thiophene- and -Furan-dicarboxylic Acid by Sulfur Tetrafluoride

Run No.	X=	SF_4 (eq.)	HF (ml)	Temp. (°C)	Time (h)	Yield(%)			
						3	4	5	6
1	S	3.5	20	100	20	51.8	10.5	-	-
2	S	5.0	20	130	20	-	69.2	-	-
3	O	3.5	8	100	20	37.8	5.1[a]	3.6[a]	9.9[a]
4	O	5.0	8	130	20	-	-	24.0	-
5	O	5.0	-	180	48	3.8	53.2	-	-

[a] Calculated from GLC, and others represent isolated yields.

The reaction conditions and yields are shown in Table I. Addition of fluorine atoms to the thiophene ring never occurred at 130°C even if anhydrous HF was added, and only 2,5-bis(trifluoromethyl)thiophene (4a) was obtained in 69% yield (run 2). At lower temperature (100°C) and SF_4 ratio (3.5 equivalent), 5-trifluoromethyl-2-thiophenecarboxylic acid (3a) was obtained in 52% yield (run 1). 2,5-Furandicarboxylic acid (2b) provided 5b or 6b as by-products regardless of the reaction temperature and SF_4 ratio (run 3). Further fluorination of the ring occurred only on 4b to give 5b because of the low aromaticity of the furan ring of 4b (run 4). Decarboxylation of 3 offered mono trifluoromethyl compounds (7) in 75-80% yields (Scheme 2).

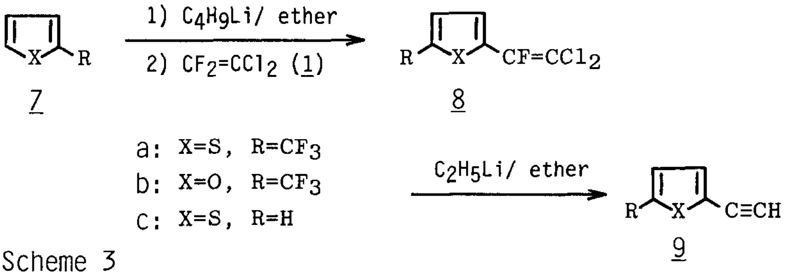


Scheme 2

Synthesis of ethynylthiophenes and ethynylfurans containing trifluoromethyl groups

We have already found a convenient route to prepare ethynylfurans, via 2,2-dichloro-1-fluorovinyl intermediates

[6]. Using a similar procedure, ethynylthiophenes and ethynylfurans were synthesized as shown in Schemes 3 and 4.

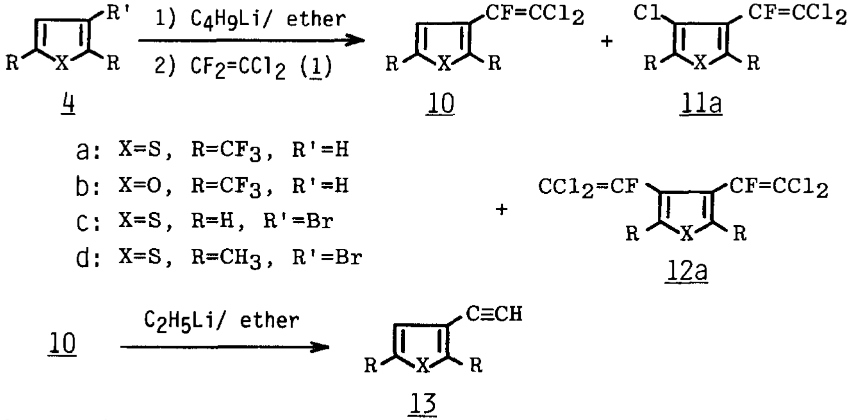


a: X=S, $R=CF_3$
b: X=O, $R=CF_3$
c: X=S, R=H

Scheme 3

Both 2-(trifluoromethyl)-thiophene and -furan (7) were directly converted to the corresponding lithio compounds without the need to make bromo compounds, and the lithiation occurred only at the α-position (5-position). Since the reaction of 2,5-bis(trifluoromethyl)thiophene (4a) gave both 11a and 12a, an inverse addition method was used to synthesize 10a.

Reaction of 2,5-bis(trifluoromethyl)furan (4b) with *n*-butyllithium gave vinyl compound (10b) in quite low yield (7 - 10%) and isolation of pure 10b was impracticable owing to formation of many by-products, which might arise from the 2,5-addition of *n*-butyllithium to the furan ring of 4b followed by telomerization. As these side reactions happened for 4b alone, analogously to the formation of 5b, they could be explained by the low aromaticity of 4b.



a: X=S, $R=CF_3$, R'=H
b: X=O, $R=CF_3$, R'=H
c: X=S, R=H, R'=Br
d: X=S, $R=CH_3$, R'=Br

Scheme 4

Polymerization of ethynylthiophenes and ethynylfurans

In the previous papers [4, 5], we have described that the ring-substituted phenylacetylenes containing trifluoromethyl groups were polymerized by transition metal catalysts such as WCl_6, and formed high molecular weight polymers. We have now found that 3-ethynylthiophene having trifluoromethyl groups at the 2,5-positions also gives high molecular weight polymers in a similar manner. The polymerization conditions, yields and molecular weights are shown in Tables II - V.

Poly(13a) was totally or partly insoluble in THF, but completely soluble in fluorocompounds such as Freon 113 and p-bis(trifluoromethyl)benzene (BTFB). Intrinsic viscosities of the polymers were measured in BTFB (Table VI). The viscosities [η] in BTFB varied inversely as the solubilities in THF, and insolubility of poly(13a) in THF was considered to be due to high molecular weight of the polymer.

The polymerizations by the tungsten complex (Systems A and B: Tables II and III) had the same tendency in the yields and molecular weights, but the tantalum complex (System C) was inactive as a polymerization catalyst (Table IV). By using tungsten complexes, all 3-ethynylthiophenes synthesized (13) gave higher molecular weight polymers (10^4 $\overline{Mw}$), while 2-ethynylthiophenes (9) except 9c, formed no polymers. The

TABLE II

Polymerization by $W(CO)_6$-CCl_4-$h\nu$ (A)[a]

Monomer	$[M]_0$ (mol/l)	$W(CO)_6$ (mmol/l)	Yield (%)	$\overline{Mw}$[b] ($\times 10^4$)	$\overline{Mn}$[b] ($\times 10^4$)	$\overline{Mw}/\overline{Mn}$
9a	0.23	56.9	0	-	-	-
9b	0.25	56.8	0	-	-	-
9c	0.37	56.8	21	1.9	0.48	3.6
13a	0.16	56.8	85[c]	1.1	0.73	1.6
13c	0.37	56.8	25	1.2	0.48	2.5
13d	0.29	56.8	90	2.1	1.1	1.9

[a] Polymerized in carbon tetrachloride at 30°C for 24h.

[b] Weight-average molecular weight ($\overline{Mw}$) and number-average molecular weight ($\overline{Mn}$) determined by GPC. [c] Partly soluble in THF.

polymerization of 13 was particularly improved by the introduction of substituents, but in polymerization of 9, the trifluoromethyl group reduced polymerizability of ethynyl thiophenes.

TABLE III

Polymerization by WCl_6-Ph_4Sn (B)[a]

Monomer	Yield (%)	$\overline{Mw}$[b] ($x10^4$)	$\overline{Mn}$[b] ($x10^4$)	$\overline{Mw}/\overline{Mn}$
9a	0	-	-	-
9b	0	-	-	-
9c	5	0.45	0.21	2.1
13a	96[c]	-	-	-
13c	89	2.56	1.02	2.5
13d	27	1.66	0.68	2.4

[a] Polymerized in toluene at 30°C for 24h: $[M]_0$=0.50(mol/l) $[WCl_6]_0$=$[Ph_4Sn]_0$=10(mmol/l). [b] Weight-average molecular weight ($\overline{Mw}$) and number-average molecular weight ($\overline{Mn}$) determined by GPC.
[c] Totally insoluble in THF.

TABLE IV

Polymerization by $TaCl_5$ (C)[a]

Monomer	Yield (%)	$\overline{Mw}$[b] ($x10^4$)	$\overline{Mn}$[b] ($x10^4$)	$\overline{Mw}/\overline{Mn}$
9a	0	-	-	-
9b	0	-	-	-
9c	7.2	0.48	0.21	2.3
13a	0	-	-	-
13c	0	-	-	-
13d	0	-	-	-

[a] Polymerized in toluene at 30°C for 24h: $[M]_0$=1.0(mol/l) $[TaCl_5]_0$=20(mmol/l). [b] Weight-average molecular weight ($\overline{Mw}$) and number-average molecular weight ($\overline{Mn}$) determined by GPC.

This difference of polymerizabilities between 9 and 13 may be derived partly from inactivation of catalyst metals by sulfur atoms. Thus the propagating ends of poly(3-ethynylthiophene)s are apart from the sulfur atoms, therefore sulfur does not seem to react as a catalytic poison.

In γ-ray induced polymerization (System D: Table V), 13a, which has two trifluoromethyl groups, only gave high molecular weight polymer, while other acetylenes synthesized gave no polymers.

TABLE V

γ-Ray Induced Polymerization[a] (D)

Monomer	Yield (%)	$\overline{Mw}$[b] ($x10^4$)	$\overline{Mn}$[b] ($x10^4$)	$\overline{Mw}/\overline{Mn}$
9a	0	-	-	-
9b	0	-	-	-
9c	3.0	0.14	0.10	1.4
13a	30[c]	0.88	0.68	1.3
13c	0.9	-	-	-
13d	0.7	-	-	-

[a] Polymerized by γ-ray (Co^{60} 40 Mrad) at ambient temperature.
[b] Weight-average molecular weight ($\overline{Mw}$) and number-average molecular weight ($\overline{Mn}$) determined by GPC. [c] Partly insoluble in THF.

TABLE VI

Intrinsic Viscosities [η] of Poly(13a) in BTFB[a] at 30°C

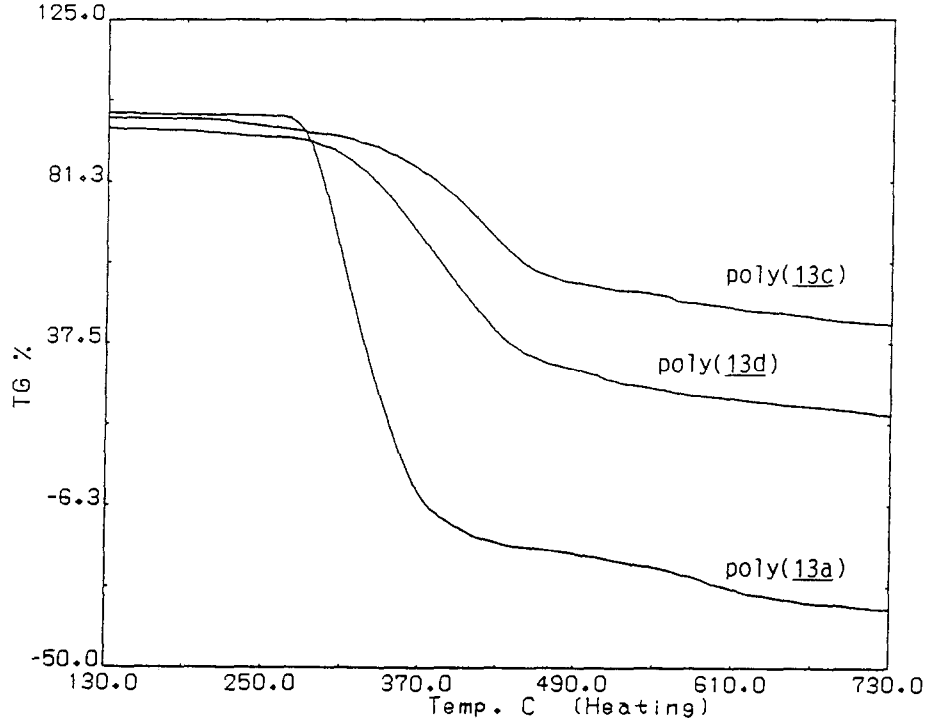
Polymer	$W(CO)_6$-CCl_4 (A)	WCl_6-Ph_4Sn (B)	γ-ray (D)
Soluble part in THF	5%	0%	62%
[η] (dl/g)	0.21	0.52	0.091

[a] All polymers were completely soluble in BTFB.
[BTFB: 1,4-bis(trifluoromethyl)benzene]

Substituent effects of the trifluoromethyl group on the thermal stability

Thermal decomposition temperatures (Td) of poly(phenylacetylene)s have been reported to be increased by the introduction of trifluoromethyl groups to the benzene ring [3]. The ethynylthiophenes synthesized were examined in a similar manner. TG curves of 13a, 13c and 13d are shown in Fig. 1, Td values in Table VII.

Td values of polyacetylenes from substituted 3-ethynylthiophenes increased in the following order, 13c<<13d=13a, and the weight losses decreased, 13c<13d<13a, independent of polymerization methods. Introduction of substituents increased Td values regardless of species of substituent. Polyacetylenes having trifluoromethyl groups decomposed more rapidly than those with methyl groups.



[in nitrogen atmosphere, heating rate 20°C/min]

Fig.1. Thermogravimetric analysis of poly(ethynylthiophene)s poly(13) made by $W(CO)_6$-CCl_4-hν system (method A).

TABLE VII

Thermal Decomposition Points of Polymers (°C)

Polymer	$W(CO)_6$-CCl_4 (A)	WCl_6-Ph_4Sn (B)	$TaCl_5$ (C)	γ-ray (D)
poly(9c)	229	211	199	-
poly(13a)	278	287	-	282
poly(13c)	215	261	-	-
poly(13d)	292	301	-	-

EXPERIMENTAL

GC-MS spectra were recorded on a Shimadzu GC-MS 7000 instrument (EI 70eV, column: SP-1000 2m or OV-17 2m). Other analytical methods and instrumentation have been described previously [3].

Materials

Ethereal solutions of an alkyllithium were prepared from corresponding alkylbromides and lithium metal in anhydrous diethyl ether, and the reactions using alkyllithium were carried out under an argon atmosphere. 1,1-Dichloro-2,2-difluoroethylene (1) was prepared by isomerization of Freon 112 and subsequent dehalogenation [10]. 2,5-Thiophenedicarboxylic acid (2a) was prepared by oxidation of 2,5-bis-(hydroxymethyl)thiophene, which was prepared from 2,5-bis-(chloromethyl)thiophene [11]. 2,5-Furandicarboxylic acid (2b) was obtained by dehydration and cyclization of mucic acid [12]. 2-Ethynyl thiophene (9c) [10] and 3-ethynyl thiophene (11c) [2] were prepared as described in the previous papers respectively. Other reagents were all commercially obtained, and used without further purification.

Fluorination of 2,5-thiophenedicarboxylic acid (2a) by sulfur tetrafluoride in the presence of hydrogen fluoride (run 1)

A mixture of 2,5-thiophenedicarboxylic acid (2a) (21.1g, 0.123mol) and anhydrous hydrogen fluoride (20ml) was placed in a 100ml autoclave made of hastelloy C. Into the autoclave cooled by liquid nitrogen, sulfur tetrafluoride (45.9g, 0.425 mol) was added under reduce pressure, and then the autoclave was heated at 100°C for 20h. After the autoclave was cooled to ambient temperature, gaseous products were released. The residual contents was poured into a mixture of ice and diethyl ether. The ether layer was separated and washed with 10% KOH solutions, and was dried over anhydrous Na_2SO_4. The ether solution was evaporated, and distilled to yield 2,5-bis-(trifluoromethyl)thiophene (4a) (2.84g, 10.5%).

In the alkaline water layer, remained 5-trifluoromethyl-2-thiophenecarboxylic acid (3a). The KOH aqueous solution extracts combined were heated at 70-80°C with activated carbon, and then the precipitate was filtered off. As the filtrate was acidified again by conc. HCl, a white precipitate was formed, and was collected. Crude precipitate was recrystallized from hot hexane to yield 3a (12.5g, 51.8%).

2,5-Bistrifluoromethylthiophene (4a)

bp. 94°C; MS m/e (relative intensity), 220 (84) M^+, 201 (100) $[M - F]^+$, 170 (43) $[M - CF_2]^+$, 151 (87) $[M - CF_3]^+$; ^1H-NMR, 7.49(s,ring); ^{19}F-NMR, 22.50(s,CF_3); Elemental analysis, Found C,33.03%, H,0.82%, Calcd. as $C_6H_2SF_6$, C,32.74%, H,0.92%; (Lit. [13]).

5-Trifluoromethyl-2-thiophenecarboxylic acid (3a)

nc; mp.79°C; ^1H-NMR, 11.23(CO_2H), 7.84(m,ring), 7.45(m,ring); ^{19}F-NMR, 22.26(s,CF_3); Elemental analysis, Found C,36.92%, H,1.41%, Calcd. as $C_6H_3O_2SF_3$, C,36.74%, H,1.54%.

Fluorination of 2,5-furandicarboxylic acid (2b) by sulfur tetrafluoride in the presence of hydrogen fluoride

The following products were obtained from 2b in a similar procedure as above.

2,5-Bistrifluoromethylfuran (4b) (run 3)

bp.63°C (Lit. 70.5-71°C [8]); MS m/e (relative intensity), 220 (84) M^+, 201 (100) $[M - F]^+$, 170 (43) $[M - CF_2]^+$, 151 (87) $[M - CF_3]^+$; ^1H-NMR, 7.41(s,ring); ^{19}F-NMR, 22.50(s,CF_3).

5-Trifluoromethyl-2-furancarboxylic acid (3b) (run 5)

mp.115°C (sublimed) (Lit. 118-119°C [8]); Elemental analysis, Found C,40.29%, H,1.39%, Calcd. as $C_6H_3O_3F_3$, C,40.02%, H,1.68%.

2,5-Difluoro-2,5-bis(trifluoromethyl)-2,5-dihydrofuran (5b)

(cis trans mixture) (run 4)

bp.80°C (Lit. 87.5°C [9]); MS m/e (relative intensity), 223 (9) $[M - F]^+$, 203 (5) $[M - 2F - H]^+$, 195 (5) $[M - F - CO]^+$, 173 (100) $[M - CF_3]^+$; ^{1}H-NMR, 6.57(s,ring); ^{19}F-NMR, -4.22 (s,CF_3), -4.22(s,CF_3), -34.30(s,F), -42.54(s,F).

2-Trifluoromethylthiophene (7a)

To a solution of recrystallized 3a (12.0g, 0.061mol) in quinoline (25ml), was added copper powder (1.7g, 0.27g-atom), and heated up to 190-200°C. The reaction mixture turned black at about 120°C, and then colorless liquid was distilled accompanying the evolution of carbon dioxide above 180°C. The fractional distillation of the liquid product yielded 7a (6.2g, 67%).

7a: bp. 95°C; MS m/e (relative intensity), 152 (100) M^+, 133 (97) $[M - F]^+$, 102 (50) $[M - CF_2]^+$; ^{1}H-NMR, 7.39(m,ring), 7.02(m,ring); ^{19}F-NMR, 19.38(s,CF_3); Elemental analysis, Found C,39.60%, H,1.76%, Calcd. as $C_5H_3SF_3$, C,39.47%, H,1.99%;(Lit. [13]).

2-Trifluoromethylfuran (7b)

By a similar procedure to 7a, 7b was obtained in 78% yield from 3b.

7b: bp. 50°C (Lit. 58°C [8]); MS m/e (relative intensity), 136 (100) M^+, 117 (45) $[M - F]^+$, ^{1}H-NMR, 7.48(s), 6.75(br), 6.44(br); ^{19}F-NMR, 14.03(s,CF_3).

2-(2',2'-Dichloro-1'-fluorovinyl)-5-trifluoromethylthiophene (8a)

To a stirred solution of 2-trifluoromethylthiophene (7a) (10.0g, 0.066mol) in anhydrous diethyl ether (25ml), cooled at -50°C by a dry ice-ethanol bath, was added ethereal *n*-butyllithium (43ml, 0.068mol). After the reaction mixture was stirred for 2h at -50°C, 1,1-dichloro-2,2-difluoroethylene (1) (13g, 0.098mol) was added dropwise into the solution, whilst maintaining the reaction temperature below -55°C. The reaction mixture was stirred for an additional 1h, and then was poured into a mixture of conc. HCl and crushed ice, and extracted with ether. The extract was washed with aqueous $NaHCO_3$ solution and water, and dried over anhydrous Na_2SO_4. After the ether layer was evaporated, the residual liquid was distilled to yield 8a (10.9g, 62%).

8a: nc; bp. 108°C(30mmHg); MS m/e (relative intensity), 268, 266,264 (100) M^+; ^{1}H-NMR, 7.41(s,ring); ^{19}F-NMR, 22.92 (s, CF_3), -22.30(s,F); Elemental analysis, Found C,31.41%, H,0.56%, Calcd. as $C_7H_2SF_4Cl_2$ C,31.72%, H,0.56%.

2-(2',2'-Dichloro-1'-fluorovinyl)-5-trifluoromethylfuran (8b)

By a similar procedure to 8a, 8b was obtained in 78% yield from 7b.

8b: nc; Yield 70%; bp. 90°C(40mmHg); MS m/e (relative intensity), 250,248 (100) M^+, 231,229 (13) $[M - F]^+$, 153,151 (89) $[M - CF_2]^+$; ^{1}H-NMR, 6.87(br,ring); ^{19}F-NMR, 13.91(s,CF_3), -35.05 (s,F); Elemental analysis C,33.85%, H,0.64%, Calcd. as $C_7H_2OF_4$ C,33.78%, H,0.81%.

2,5-Bis(trifluoromethyl)-3-(2',2'-dichloro-1'-fluorovinyl) thiophene (10a) (inverse addition method)

To a solution of 4a (22.9g, 0.104mol) in anhydrous diethyl ether (30cc) cooled below -55°C, was added ethereal n-butyllithium (95ml, 0.149mol). Then the reaction mixture was stirred at -30°C for 2h, and was dropped into 1 (84g,0.63mol) in an another flask by the inverse addition method, whilst maintaining the temperature below -50°C. The reaction mixture was poured into an aqueous HCl solution, and then the ether layer was separated, washed with aqueous $NaHCO_3$ solution and water. GC and GC-mass analyses of the ether layer showed three products (10a:11a:12a=25:1.4:1). The main product 10a was isolated by fractional distillation in 39% yield.

10a: nc; bp. 88°C(30mmHg); MS m/e (relative intensity), 336, 334,332 (78) M^+, 317,315,313 (21) $[M - F]^+$, 299,297 (100) $[M - Cl]^+$, 262 (28) $[M - 2Cl]^+$; ^{1}H-NMR, 7.65(t,ring,J=1.1Hz); ^{19}F-NMR, 22.93(d,CF_3,J=13.0Hz), 21.91(s,CF_3), -13.11(q,F, J=11.2 Hz); Elemental analysis, Found C,28.94%, H,0.26%, Calcd. as $C_8HSF_7Cl_2$ C,28.85%, H,0.30%.

11a: MS m/e (relative intensity), 370,368,366 (100) M^+, 349, 347 (15) $[M - F]^+$, 333,331 (92) $[M - Cl]^+$, 298,296 (30) $[M - 2Cl]^+$.

12a: MS m/e (relative intensity), 414,412,410 (34) M^+, 377,375 (24) $[M - Cl]^+$, 342,340 (48) $[M - 2Cl]^+$, 307,305 (100) $[M - 3Cl]^+$.

2,5-Dimethyl-3-(2',2'-dichloro-1'-fluorovinyl)thiophene (10d)

To a solution of 2,5-dimethyl-3-bromothiophene (4d) (18.2g, 0.095mol) in anhydrous diethyl ether (50ml) cooled at -30°C, was added ethereal *n*-butyllithium (65ml, 0.103mol). After stirring for 1h, 1 (21g, 0.16mol) was dropped into the reaction mixture below -50°C. The reaction mixture was treated using the above mentioned procedure to give 10d (13.5g, 63%).

10d: nc; bp. 100°C(8mmHg); MS m/e (relative intensity), 228, 226,224 (82) M^+, 211,209 (9) $[M - CH_3]^+$, 191,189 (100) $[M - Cl]^+$, 154 (39) $[M - 2Cl]^+$, 153 (30) $[M - 2Cl - H]^+$; ^{1}H-NMR, 6.71(br,ring), 2.41(s,C^5H_3), 2.38(s,C^2H_3); ^{19}F-NMR, -11.89 (s,F); Elemental analysis, Found C,42.63%, H,3.05%, Calcd. as $C_8H_7SFCl_2$ C,42.68%, H,3.13%.

2-Ethynyl-5-trifluoromethylthiophene (9a)

To a solution of 8a (12.9g, 0.049mol) in anhydrous diethyl ether (25ml) cooled below -55°C, was added ethereal ethyllithium (80ml,0.113mol). The reaction mixture was stirred for 30 min, and then was poured into ice-water acidified with conc. HCl. The ether layer was separated, washed with aq. $NaHCO_3$ solution and water. The ether layer was dried over Na_2SO_4, and distilled to yield 9a (5.5g, 62%).

9a: nc; bp. 70°C(90mmHg); MS (relative intensity), 176 (100) M^+, 157 (33) $[M - F]^+$, 126 (32) $[M - CF_2]^+$; ^{1}H-NMR, 7.25,7.23 (br,ring), 3.40(s,C≡CH); ^{19}F-NMR, 22.92(s,CF_3); Elemental analysis, Found C,47.69%, H,1.63%, Calcd. as $C_7H_3SF_3$ C,47.72%, H,1.72%.

The following acetylenes were synthesized from corresponding vinyl compounds by a similar procedure to that for 9a.

2-Ethynyl-5-trifluoromethylfuran (9b)

nc; Yield 64%; bp. 82°C; MS m/e (relative intensity), 160 (100) M^+, 141 (19) $[M - F]^+$, 110 (13) $[M - CF_2]$; ^{1}H-NMR, 6.75 - 6.63(m, ring), 3.42(s, C≡CH); ^{19}F-NMR, 14.31(s,CF_3); Elemental analysis C,52.74%, H,1.80%, Calcd. as $C_7H_3OF_3$ C,52.52%, H,1.89%.

2,5-Bis(trifluoromethyl)-3-ethynylthiophene (13a)

nc; Yield 64%; bp. 73°C(100mmHg); MS m/e (relative intensity), 244 (100) M^+, 255 (56) $[M - F]^+$, 194 (19) $[M - CF_2]$, 175 (80) $[M -CF_3]^+$; ^{1}H-NMR, 7.47(br,ring), 3.36(s,C≡CH); ^{19}F-NMR, 21.93 (s,CF_3), 21.66(s,CF_3); Elemental analysis C,39.11%, H,0.72%, Calcd. as $C_8H_2SF_6$ C,39.35%, H,0.83%.

2,5-Dimethyl-3-ethynylthiophene (13d)

nc; Yield 43%; bp. 68°C(12mmHg); MS m/e (relative intensity), 136 (100) M^+, 135 (75) $[M - H]^+$, 121 (36) $[M - CH_3]$; ^{1}H-NMR, 6.60(br,d,ring), 3.09(s,C≡CH) 2.45 (s,CH_3), 2.35(s,CH_3); Elemental analysis C,70.57%, H,5.70%, Calcd. as C_8H_8S C,70.54%, H,5.92%.

Reaction of 2,5-bis(trifluoromethyl)furan (4b) with n-butyllithium and 1,1-dichloro-2,2-difluoroethylene (1)

To a solution of 4b (20.0g, 0.098mol) in anhydrous diethyl ether (50ml) was added ethereal *n*-butyllithium (85ml, 0.587mol) below -55°C, and then the reaction mixture was stirred at -20°C for 2h. The reaction mixture was dropped into 1 (78.0g, 0.587mol) by the inverse addition method, maintaining the reaction temperature below -50°C. The reaction mixture was poured into an aqueous HCl solution, and then the ether layer was separated, washed with aqueous $NaHCO_3$ and water. The ether layer was dried over Na_2SO_4, and distilled to remove ether. GC and GC-mass analyses of the residue showed many by-products, therefore the desired product 10b (2.29g, 7.36% GC calculated) could not be isolated by fractional distillation.

10b: MS m/e (relative intensity),320,318,316 (100) M^+, 299,297 (24) $[M - F]^+$, 283,281 (60) $[M - Cl]^+$.

Polymerization of ethynylthiophenes and ethynylfurans

Polymerization methods were carried out according to the previously reported procedures [3], using the following systems:

(1) $W(CO)_6$-CCl_4-hν irradiation system (method A)
(2) WCl_6-Ph_4Sn system (method B)
(3) $TaCl_5$ system (method C)
(4) γ-ray induced polymerization (method D)

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