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SYNTHESIS AND POLYMERIZATION OF SOME ETHYNYL TRIFLUOROMETHYL NAPHTHALENES

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SUMMARY

Some bromonaphthoic acids were fluorinated with SF_4 to bromo(trifluoromethyl)naphthalenes. Although a reaction of Grignard reagent of one of the bromides with $Cl_2C=CF_2$ gave low yield of a (dichlorofluorovinyl)(trifluoromethyl)naphthalene, lithio derivatives gave the desired ethynyl(trifluoromethyl)-naphthalenes in improved yields after subsequent eliminations of the vinylic halogens with n-butyllithium. Polymerization of the acetylenes was carried out with photo-activated $W(CO)_6$ catalyst to yield high-molecular-weight polymers.

INTRODUCTION

We have recently reported the syntheses of some fluorine-containing aromatic acetylene compounds and their polymerizations [1]. In this paper, we report the synthesis of some ethynyl(trifluoromethyl)naphthalenes (1a-d) and their polymerization. Okuhara reported the preparation of 1-ethynyl-naphthalene from Grignard reagent of 1-bromonaphthalene with $Cl_2C=CF_2$ (2) [2]. However, some different reactivities were

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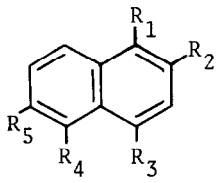
observed in the similar reactions of bromo(trifluoromethyl)-naphthalenes (3a-d). Photochemically activated $W(CO)_6$ catalyst effected the polymerization of the naphthylacetylenes 1 to high-molecular-weight polymers.



	1a	1b	1c	1d	3a	3b	3c	3d
R_1	C≡CH	C≡CH	C≡CH	C≡CH	Br	Br	Br	Br
R_2	H	CF_3	H	H	H	CF_3	H	H
R_3	CF_3	H	H	H	CF_3	H	H	H
R_4	H	H	CF_3	H	H	H	CF_3	H
R_5	H	H	H	CF_3	H	H	H	CF_3

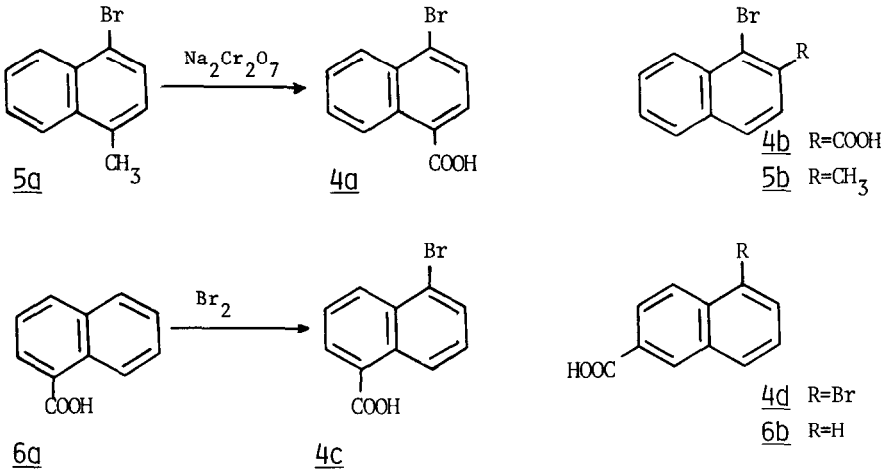
RESULTS AND DISCUSSION

(I) Preparation of Bromo(trifluoromethyl)naphthalenes (3).

4-Bromo-1-naphthoic acid (4a) was prepared from 1-bromo-4-methylnaphthalene (5a) [3] by bichromate oxidation in 43 % yield. Similarly, 1-bromo-2-naphthoic acid (4b) was prepared from 1-bromo-2-methylnaphthalene (5b) (31 %) [4].

Bromination of 1-naphthoic acid (6a) gave only 5-bromo-1-naphthoic acid (4c) [5]. However, bromination of 2-naphthoic acid (6b) did not give the pure 5-bromo-2-naphthoic acid (4d), probably because of contamination by an isomer brominated at another position, though there were reports that claimed the reaction had given only 5- brominated product [5,6]. Thus, 4d had to be purified by successive recrystallizations of its methyl ester followed by alkaline hydrolysis again to 4d. (Scheme I)

Fluorination of these bromonaphthoic acids 4 was carried out by sulfur tetrafluoride in anhydrous hydrogen fluoride at 70°C for 20 h in an autoclave to afford bromo(trifluoromethyl)-



Scheme I

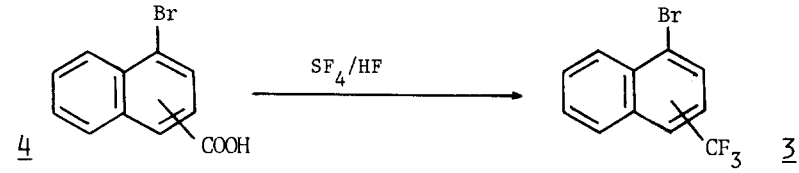
naphthalenes (3a-d) in moderate yields (Table I). Addition of HF lowered the reaction temperature in comparison with the fluorination of nitronaphthoic acids [7]. At a higher reaction temperature, no expected product was isolated from the intractable tar (Table I, 4b). The methyl ester of 4d also gave no trifluoride 3d.

(II) Introduction of Ethynyl Group into Trifluoromethylnaphthalenes.

In a previous paper [2], the reaction of α-naphthyl magnesium bromide and 1,1-dichloro-2,2-difluoroethylene (2) was reported to give good yield of the dichlorofluorovinylated product in spite of the lower yield of the similar reaction of the olefin 2 and α-naphthyllithium. However, the Grignard reagent of trifluoromethyl derivative 3a afforded the corresponding substitution product 7a in low yield (15 %) due to an unexpected coupling reaction to the binaphthyl 8 (26 %) (Scheme II). This change of the reactivity was probably caused by the introduction of an electron-withdrawing trifluoromethyl group. A more suitable reaction which gave higher yields and selectivity was lithiation with n-butyllithium (diethyl ether

TABLE I

Fluorination of Bromonaphthoic acids 4 to Bromo-(trifluoromethyl)naphthalenes 3

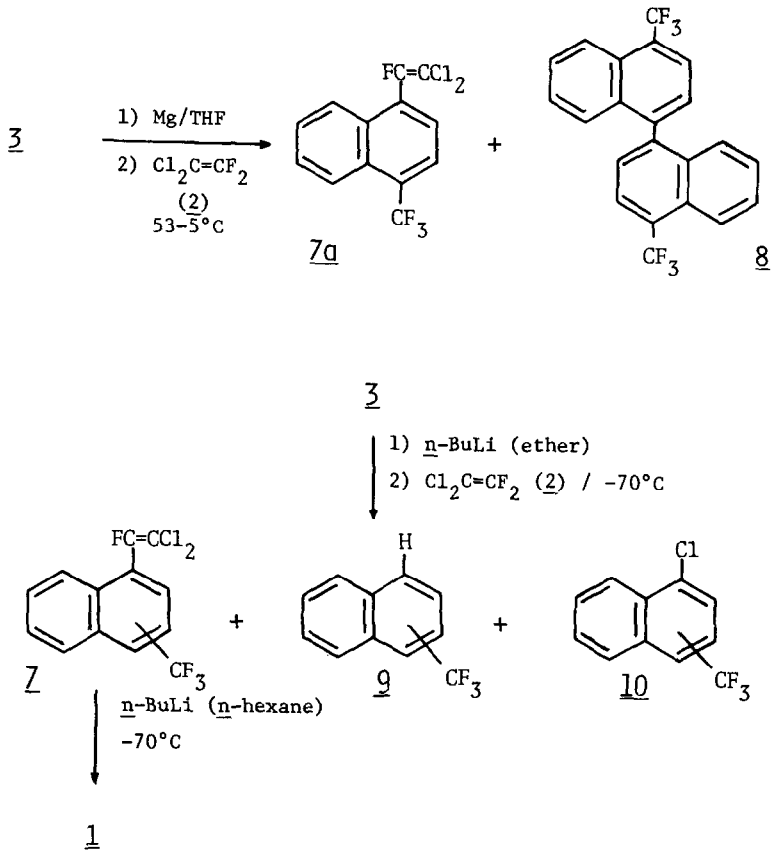


4 3

Acid	Product	Reaction Temp.	Yield	mp (bp)
4a	3a	70°C	66 %	bp; 96-8°C/4 mm
		90°C	77 %	
4b	3b	70°C	66 %	mp; 61-3°C
		130°C	-[a]	
4c	3c	70°C	62 %	mp; 37-8.5°C
4d	3d	50°C	38 %	bp; 106-7°C/5 mm
		70°C	48 %	
		80°C[b]	-[a]	

[a] No identifiable product. [b] Methyl ester of 4d.

solution) in ether at -70°C and subsequent slow addition of dichlorodifluoroethylene 2 at the same temperature. In this way, bromo(trifluoromethyl)naphthalenes 3 were converted to the acetylene precursors 7 although the by-products, (trifluoromethyl)naphthalenes 9 and chloro(trifluoromethyl)naphthalenes 10, were not separable (7 : 9 : 10 = 9 : 1 : 1) (Scheme II). The reaction times were similar (1 h at -70°C) in each case except for 3b which required a longer time (2 h at -70°C) because the reactivity was decreased by steric hindrance. Higher reaction temperature or use of n-butyllithium in n-hexane solution causes the decrease of the selectivity due to increase in the ratio of the halogen exchanged products 10 and the protonated (trifluoromethyl)naphthalenes 9.



Scheme II.

TABLE II

Conversion of Bromo(trifluoromethyl)naphthalenes 3
to Ethynyl(trifluoromethyl)naphthalenes 1

Bromide	Acetylene	Yield	^{1}H-NMR(CCl_4)
3a	1a	48 %	3.49 (s, 1H), 7.4-8.6 (m, 6H)
3b	1b	47 %	3.70 (s, 1H), 7.4-8.5 (m, 6H)
3c	1c	60 %	3.34 (s, 1H), 7.1-8.6 (m, 6H)
3d	1d	69 %	3.36 (s, 1H), 7.2-8.5 (m, 6H)

Conversion of these precursor olefins 7 to acetylenes 1 was performed by treatment of the resulting products mixtures with 2-molar amounts of n-butyllithium (n-hexane solution) in ether at -70°C, the reaction mixtures being separated by preparative HPLC (SiO_2, n-hexane). Yields of the acetylenes 1 were 47-69 % from the corresponding bromides 3 (Table II).

(III) Polymerization of the Acetylenes 1.

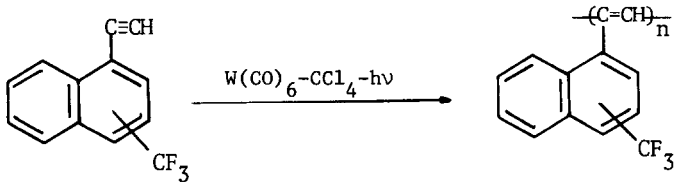
Although polymerizations of substituted acetylenes do not always give higher-molecular-weight polymers, Masuda et al. have reported efficient transition metal catalysts for converting mono- or disubstituted acetylenes into high-molecular-weight polyacetylenes [8]. Recently, we reported that photochemically activated $W(CO)_6$ in CCl_4 was effective for polymerization of (trifluoromethyl)phenylacetylenes [1a]. Polymerization of the (trifluoromethyl)naphthylacetylenes 1 was also achieved with the same catalyst in CCl_4 at 30°C. For comparison, α-naphthylacetylene was also polymerized under the same conditions. In Table III, the reaction conditions, yields and molecular weights of the formed polymers are summarized.

Yields of polymerization of the naphthylacetylene monomers were more than 90 % at appropriate monomer and catalyst concentrations except for monomer 1b, which gave no polymer under the given reaction conditions. The decrease of the polymerizability of 1b was affected by the steric hindrance of the two o- position substituents. Such reduced polymerizability was also observed in the case of 2,6-bis(trifluoromethyl)phenylacetylene [9]. Masuda has reported on the steric effects of the monomer acetylenes that prevents their cyclotrimerization to give benzene derivatives [8]. However, there seems to be a limitation of bulkiness of the monomers which polymerize with the transition metal catalysts.

Molecular weight of the polymer is a function of the monomer as shown in Table III. Especially, the naphthylacetylenes with a trifluoromethyl group tend to afford polymers which have similar or higher molecular weight than the parent naphthylacetylene. Similar results were observed in the

TABLE III

Polymerization of Ethynylnaphthalenes 1.



Monomer	[M] mol/l	$W(CO)_6$ mmol/l	Yield (%)	Mn x 10^3	Mw x 10^3
1-ethynyl-naphthalene	0.67	60	96	12.1	39.4
1a	0.33	60	100	32.6	108
1b	0.30	60	0	—	—
1c	1.09	60	77	20.2	46.3
	0.49	60	97	11.7	30.2
	0.065	60	44	9.9	35.1
	0.49	6	12	66.9	181
1d	0.55	60	93	42.5	147

polymerization of (trifluoromethyl)phenylacetylene and the parent phenylacetylene [1a,8]. In the polymerization of 1c, it was observed that the molecular weight increased with increasing monomer concentration and with decreasing catalyst concentration. Similar results were obtained in the polymerization of o-(trifluoromethyl)phenylacetylene [1a]. Thermal stabilities of the fluorinated polymers were all comparable to the parent polynaphthylacetylene (decomposition temperature; Td = 291-344°C in air or in N_2) and the apparent effect of introduction of trifluoromethyl group was not found; see experimental.

As described above, some novel ethynyl(trifluoromethyl)-naphthalenes were prepared from the corresponding bromonaphthoic acids and polymerized with $W(CO)_6$ catalyst to high-molecular-weight polymers except for the sterically hindered 2-trifluoromethyl derivative 1b.

EXPERIMENTAL

Melting points were taken in a sealed tube on a Mitamura Riken's micro melting point measurement apparatus and were uncorrected. IR spectra were obtained on a JASCO IR-810 infrared spectrophotometer. ^1H- and ^{19}F-NMR spectra were recorded on a Hitachi R-22 instrument at 90 MHz and a Hitachi R-20B instrument at 56.45 MHz, respectively, and chemical shifts were reported in parts per million (δ) relative to Me_4Si as an internal standard for ^1H and to CF_3COOH as an external standard for ^{19}F. Mass spectra and GC-MS analyses were performed on a Shimazu GC-MS 7000 (column; 2 m column packed with silicone OV-17). n-Butyllithium (ether solution) was prepared by Okuhara's procedure [2]. All reactions of n-butyllithium were conducted under nitrogen atmosphere, with uses of sodium-dried ether. The molecular weights of polymers were estimated with a Toyo Soda HLC-802A GPC (THF), and the calibration curve for polystyrene was used to calculate the molecular weights. Decomposition temperatures (T_d) of polymers were analysed with a Seiko TG-20 thermal gravity measurement apparatus in air and in N_2.

4-Bromo-1-naphthoic acid (4a).

1-Bromo-4-methylnaphthalene (5a) (50.0 g, 0.23 mol) was dispersed in aq. $Na_2Cr_2O_7 \cdot 2H_2O$ solution (2.7 M, 150 ml), and the mixture was heated in an autoclave at 250°C for 20 h (max. 18 atm). The cooled mixture was dissolved with 1000 ml of water and then the mixture was acidified with conc. hydrochloric acid. The formed precipitates were filtered and dried. Free acid 4a was recrystallized from acetic acid (24.8 g, 43 %): mp 220-4°C (lit. 217-220°C [3a], 212°C [3b]).

1-Bromo-2-naphthoic acid (4b).

Reaction of 1-bromo-2-methylnaphthalene (5b) (50.0 g, 0.23 mol) with aq. $Na_2Cr_2O_7 \cdot 2H_2O$ solution (2.7 M, 150 ml) as described above gave acid 4b (17.9 g, 31 %): mp 182-186°C (lit. 186°C [4]).

5-Bromo-1-naphthoic acid (4c).

Bromination of 1-naphthoic acid (6a) was carried out according to Hausmann's procedure [5].

5-Bromo-2-naphthoic acid (4d).

Bromination of 2-naphthoic acid (6b) (50.0 g, 0.29 mol) did not give pure acid 4d. The mixture of brominated acids (51.9 g) was dissolved in conc. H_2SO_4 (25 ml) and methanol (500 ml), and the mixture was refluxed for 5 h. The cooled mixture was evaporated under reduced pressure to concentrate to ca. 100 ml, and was poured into water (1000 ml). After extraction of the mixture with ether, evaporation of the solvent gave a solid mixture of esters. Successive recrystallizations from methanol afforded pure methyl 5-bromo-2-naphthoate (25.5 g); mp 73-4°C (lit. 73°C [6]); IR (KBr) 1725 cm^{-1}; ^{1}NMR (CCl_4) 8.5-7.2 (m, 6H), 3.92 (s, 3H); MS, m/z (%) 266 (M^++2, 99), 264 (M^+, 100).

Methyl 5-bromo-2-naphthoate was dissolved to aq. NaOH solution (2.5 M, 250 ml), and stirred under refluxing for 3 h. The resulting clear solution was acidified with conc. HCl, yielding a precipitate which was filtered off and dried to give pure 5-bromo-2-naphthoic acid (4d) (24.0 g, 33 % from 2-naphthoic acid 6b): mp 250-5°C (lit. 270°C [6]).

General procedure for fluorination of bromonaphthoic acids.

To a mixture of a bromonaphthoic acid (4) (ca. 100 mmol) and anhydrous hydrogen fluoride (40 ml) in a 100 ml autoclave made of Hastelloy C under cooling with liquid N_2, SF_4 (43.2 g, 400 mmol) was added under reduced pressure. The reaction

vessel was heated at 70°C for 20 h (max. pressure; 16 atm). The cooled mixture was poured into ice-water and extracted with ether. The combined extracts were washed with water and aq. KOH solution, dried with Na_2SO_4, and evaporated under reduced pressure to give a residue, which was distilled under reduced pressure (3a, 3d) or recrystallized from ethanol (3b, 3c).

1-Bromo-4-(trifluoromethyl)naphthalene (3a): nc, yield 66 %; IR (neat film) 3080, 1573, 1512, 1340, 1305, 1268, 1142, 1120, 987, 840, 765 cm^{-1}; ^{1}H-NMR (CCl_4) 8.2-7.3 (m); ^{19}F-NMR (CCl_4) 18.5 (d, J=2.2 Hz); MS m/z (%) 276 (M^++2, 99), 274 (M^+, 100), 195 (M^+-Br, 92), 175 (39), 126 (29): Analysis: Found: C, 47.86; H, 2.01 %: $C_{11}H_6BrF_3$ requires C, 48.03; H, 2.20 %.

1-Bromo-2-(trifluoromethyl)naphthalene (3b): nc, yield 67 %; IR (KBr) 3060, 1600, 1465, 1337, 1786, 1248, 1155, 1130, 1100, 965, 820, 758, 745 cm^{-1}; ^{1}H-NMR (CCl_4) 7.4-8.4 (m); ^{19}F-NMR (CCl_4) 17.2 (s); MS m/z (%) 276 (M^++2, 98), 274 (M^+, 100), 195 (M^+-Br, 97), 175 (31), 126 (27): Analysis: Found: C, 47.76; H, 2.15 %: $C_{11}H_6BrF_3$ requires C, 48.03; H, 2.20 %.

1-Bromo-5-(trifluoromethyl)naphthalene (3c): nc, yield 64 %; IR (KBr) 3070, 1573, 1503, 1310, 1232, 1202, 1155, 1140, 1115, 800, 690 cm^{-1}; ^{1}H-NMR (CCl_4) 7.2-8.4 (m); ^{19}F-NMR (CCl_4) 18.7 (d, J=2.0 Hz); MS m/z (%) 276 (M^++2, 95), 274 (M^+, 100), 195 (M^+-Br, 96), 175 (39), 145 (25), 97 (26): Analysis: Found: C, 47.93; H, 2.29 %: $C_{11}H_6BrF_3$ requires C, 48.03; H, 2.20 %.

1-Bromo-6-(trifluoromethyl)naphthalene (3d): nc, yield 49 %; IR (neat film) 3070, 1602, 1504, 1355, 1314, 1265, 1200, 1155, 1130, 1075, 892, 840, 795 cm^{-1}; ^{1}H-NMR (CCl_4) 7.3-8.3 (m); ^{19}F-NMR (CCl_4) 15.0 (s); MS m/z (%) 276 (M^++2, 95), 274 (M^+, 100), 195 (M^+-Br, 96), 175 (36), 126 (30): Analysis: Found: C, 47.81; H, 2.20 %: $C_{11}H_6BrF_3$ requires C, 48.03; H, 2.20 %.

Reaction of 1,1-dichloro-2,2-difluoroethylene (2) and the Grignard Reagent prepared from 3a.

To a stirred mixture of magnesium turnings (4.00 g, 165 mmol) and anhydrous THF (10 ml), a mixture of 3a (39.37 g, 143 mmol) and THF (300 ml) was added dropwise in 1 h under gentle

reflux. The mixture was stirred under reflux for an additional 2 h and was then red-brown. After the bromide 3a was completely consumed, several portions of 1,1-dichloro-2,2-difluoroethylene (2) (60 ml, ca. 680 mmol) were added to the solution, and the mixture was refluxed at 53-5°C for 10 h. The cooled mixture was poured into ice-water (400 ml), acidified with conc. hydrochloric acid (40 ml), and extracted with ether. The combined extract was washed with water and sat. $NaHCO_3$ solution and dried with Na_2SO_4. Removal of the solvent and chromatography on a silica gel column (n-hexane) gave 1-(2',2'-dichloro-1'-fluorovinyl)-4-(trifluoromethyl)naphthalene (7a) (6.78 g, 15 %), bis-1,1-[4-(trifluoromethyl)naphthyl] (8) (7.25 g, 26 %), and other unseparable minor fractions.

7a: nc, bp 102-6°C (3 mmHg); IR (neat film) 3070, 1655, 1594, 1522, 1318, 968, 942, 778, 762 cm^{-1}; ^{1}H-NMR (CCl_4) 8.4-7.6 (m); ^{19}F-NMR (CCl_4) 19.6 (s, 3F), -6.7 (s, 1F); MS m/z (%) 310 (M^++2, 17), 308 (M^+, 27), 275 (M^++2-Cl, 23), 273 (M^+, 65), 238 (100), 204 (28): Analysis: Found: C, 50.53; H, 1.80 %: $C_{13}H_6Cl_2F_4$ requires C, 50.52; H, 1.96 %.

8: nc, mp 152-4°C; IR (KBr) 3060, 2920, 1578, 1506, 1330, 1262, 1118, 765 cm^{-1}; ^{1}H-NMR (CCl_4) 8.5-7.3 (m); ^{19}F-NMR (CCl_4) 20.2 (s); MS m/z (%) 391 (M^++1, 24), 390 (M^+, 100), 321 (60), 320 (40), 252 (48): Analysis: Found: C, 67.70; H, 3.10 %: $C_{22}H_{12}F_6$ requires C, 67.70; H, 3.10 %.

Ethynyl(trifluoromethyl)naphthalenes (1) from Bromo(trifluoromethyl)naphthalenes (3).

To a stirred mixture of a bromo(trifluoromethyl)naphthalene (3) (10 g, 36 mmol) in anhydrous diethyl ether (100 ml), n-butyllithium in diethyl ether (1 M, 40 ml, 40 mmol) was added at -70°C in 30 min, and the resulting mixture was stirred at -70°C for additional 1 h. After completion of lithiation, 1,1-dichloro-2,2-difluoroethylene (2) (10 ml, ca. 110 mmol) was carefully added at -70°C in 15 min. The mixture was stirred at -70°C for 1 h further (2 h for 3b), and then allowed to warm to

room temperature, poured into water, acidified with conc. hydrochloric acid (2 ml), and extracted with ether. The combined extracts were washed with water and sat. $NaHCO_3$ solution and dried with Na_2SO_4. Removal of the solvent and Kugel-rohr distillation (110°C/0.2 mmHg) of the residue gave a 9:1:1 mixture of (2',2'-dichloro-1'-fluorovinyl)(trifluoromethyl)-naphthalene (7), (trifluoromethyl)naphthalene (9) (m/z 196) and chloro(trifluoromethyl)naphthalene (10) (m/z 230) as a pale yellow oil (ca. 10 g). The mixture (ca. 10 g) was dissolved in anhydrous ether (100 ml), and n-butyllithium (1.60 M n-hexane solution, 40 ml, 64 mmol) was added dropwise in 1h at -70°C to the mixture. After stirring at -70°C for 2 h, the dark blue mixture was poured into water (100 ml), acidified with conc. hydrochloric acid to pH ≃ 3, and extracted with ether. The combined extracts were washed with water, sat. $NaHCO_3$ solution, and again with water, and dried with Na_2SO_4. Evaporation of the solvent and preparative HPLC on a SiO_2 packed column (Waters Prep LC/System 500A; Prep PAK-500/SILICA) on elution with n-hexane give ethynyl(trifluoromethyl)naphthalene (1) and a mixture of (trifluoromethyl)naphthalene (9) and chloro-(trifluoromethyl)naphthalene (10).

1-Ethynyl-4-(trifluoromethyl)naphthalene (1a): nc, colorless oil; IR (neat film) 3295, 3070, 2100, 1582, 1518, 1328, 1312, 1264, 1124, 844, 764 cm^{-1}; ^{19}F-NMR (CCl_4) 19.0 (s); MS m/z (%) 221 (M^++1, 13), 220 (M^+, 100), 219 (30), 201 (26), 170 (42): Analysis: Found: C, 70.79; H, 3.32 %: $C_{13}H_6F_3$ requires C, 70.91; H, 3.20 %.

1-Ethynyl-2-(trifluoromethyl)naphthalene (1b): nc, mp 36-8°C; IR (KBr) 3305, 3070, 2115, 1598, 1472, 1345, 1298, 1175, 1130, 825, 658 cm^{-1}; ^{19}F-NMR (CCl_4) 17.1 (s); MS m/z (%) 221 (M^++1, 17), 220 (M^+, 100), 219 (33), 201 (31), 170 (35): Analysis: Found: C, 70.87; H, 3.08 %: $C_{13}H_6F_3$ requires C, 70.91; H, 3.20 %.

1-Ethynyl-5-(trifluoromethyl)naphthalene (1c): nc, colorless oil; IR (neat film) 3200, 3060, 2100, 1584, 1512, 1312, 1122, 792 cm^{-1}; ^{19}F-NMR (CCl_4) 19.5 (s); MS m/z (%) 221 (M^++1, 13), 220 (M^+, 100), 219 (31), 201 (13), 170 (42): Analysis: Found: C, 70.88; H, 3.23 %: $C_{13}H_6F_3$ requires C, 70.91; H, 3.20 %.

1-Ethynyl-6-(trifluoromethyl)naphthalene (1d): nc, colorless oil; IR (neat film) 3300, 3055, 2100, 1596, 1470, 1308, 1122, 798 cm^{-1}; ^{19}F-NMR (CCl_4) 16.7 (s): MS m/z (%) 221 (M^++1, 15), 220 (M^+, 100), 219 (30), 201 (27), 170 (25): Analysis: Found: C, 70.94; H, 3.17 %: $C_{13}H_6F_3$ requires C, 70.91; H, 3.20 %.

Polymerization of ethynylnaphthalenes (1).

A solution of $W(CO)_6$ in CCl_4 (25 ml) was irradiated with a 100-W high-pressure-mercury lamp at 30°C for 30 min, and then monomer acetylene 1 was added to this solution. Polymerization was conducted in the dark at 30°C for 24 h. The polymerization was terminated by addition of methanol (100 ml). The precipitates were filtered off and dried to constant weight.

Poly(1-ethynylnaphthalene): T_d 319°C (air), 343°C (N_2); IR (KBr) 3020, 1582, 1500, 1392, 774 cm^{-1}.

Poly[1-ethynyl-4-(trifluoromethyl)naphthalene]: T_d 291°C (air), 304°C (N_2); IR (KBr) 3000, 1578, 1508, 1325, 1105, 842, 662 cm^{-1}.

Poly[1-ethynyl-5-(trifluoromethyl)naphthalene]: T_d 306°C (air), 344°C (N_2); IR (KBr) 3000, 1580, 1508, 1305, 1112, 786, 700 cm^{-1}.

Poly[1-ethynyl-6-(trifluoromethyl)naphthalene]: T_d 321°C (air), 300°C (N_2); IR (KBr) 3020, 1626, 1588, 1464, 1302, 1106, 1070, 894, 826, 796, 755, 738 cm^{-1}.

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