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SYNTHESIS AND POLYMERIZATION OF 2,5-DISUBSTITUTED PHENYLACETYLENES CONTAINING TRIFLUOROMETHYL GROUPS

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SUMMARY

Four phenylacetylenes (2-R^2-5-R^5-$C_6H_3C{\equiv}CH$: 1a $R^2=R^5=CF_3$; 1b $R^2=CF_3, R^5=CH_3$; 1c $R^2=CH_3, R^5=CF_3$; 1d $R^2=R^5=CH_3$) were synthesized via lithio compounds or Grignard reagent. Bromo(methyl)benzotrifluorides, the precursors for the lithio compounds, were prepared by the fluorination of the corresponding benzoic acids with sulfur tetrafluoride. Polymerization using transition metal catalysts provided polyacetylenes in high yields for all the monomers, while the yields of γ-ray induced polymerization depended on the monomers. The molecular weights of polyacetylenes have a positive correlation with the yields for all the polymerizations. The substituent effects on the molecular weights and thermal stabilities of polymers obtained were discussed.

INTRODUCTION

Polyphenylacetylenes having trifluoromethyl groups and polydiphenyldiacetylenes derived from the phenylacetylenes can

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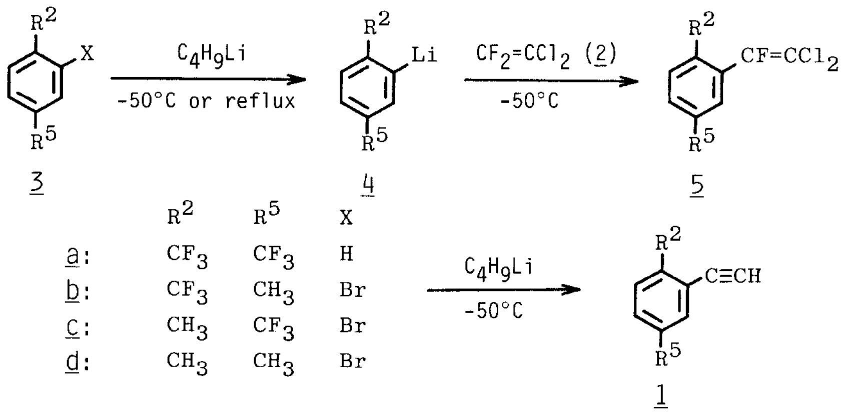
be used as various functional materials such as resists, electric conductors and nonlinear optical devices [1]. These specific properties arise from the conjugated double-bonds and trifluoromethyl group of the side chain. The trifluoromethyl group causes asymmetric distortion of the conjugated system and intramolecular charge transfer. However, when a conjugated system has both electron attracting and donating groups at opposite ends, the π-electron energy levels are greatly shifted [2]. Hence, it should be significant to study phenylacetylenes containing both electron attracting and donating substituents.

Previously, we have reported synthesis and polymerization of various substituted acetylenes containing a trifluoromethyl group, i.e., phenylacetylenes [3,4], naphthylacetylenes [5], ethynylfurans [6], and the position of the substituents was shown to affect the polymerizability and the properties of the polymer. In this paper, we describe the synthesis and polymerization of two interesting acetylenes, [methyl(trifluoromethyl)phenyl]acetylenes (1b and 1c), which have electron attracting and donating substituents at opposite ends. In addition, [2,5-bis(trifluoromethyl)phenyl]acetylene (1a) and (2,5-dimethylphenyl)acetylene (1d) were also examined in order to compare the polymerizability and the properties of the polymers with those of the [methyl(trifluoromethyl)phenyl]acetylenes.



	R^2	R^5	X
a:	CF_3	CF_3	H
b:	CF_3	CH_3	Br
c:	CH_3	CF_3	Br
d:	CH_3	CH_3	Br

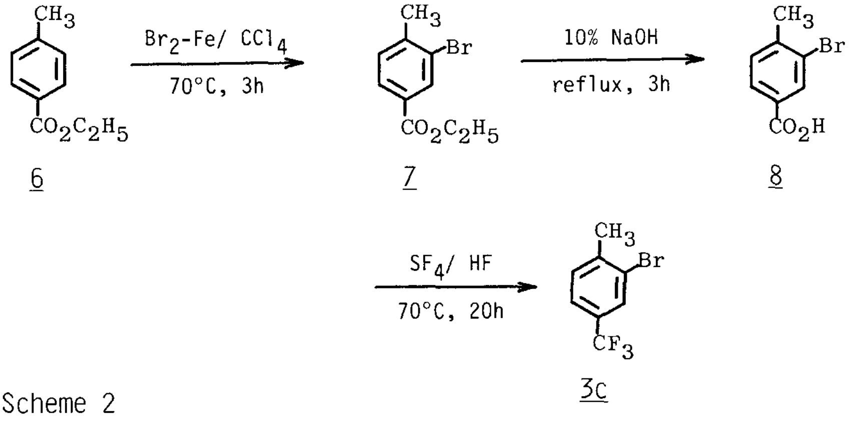
Scheme 1

RESULTS AND DISCUSSION

Preparation of monomer acetylenes

Several phenylacetylenes have been prepared by a route via 2,2-dichloro-1-fluorovinylbenzene intermediates [7,8]. Preparation of [2,5-bis(trifluoromethyl)phenyl]acetylene (1a) was carried out according to Scheme 1. Other 2,5-disubstituted acetylenes (1b-d) were also prepared in a similar manner.

Because of the difficulty of the lithiation of 4-methylbenzotrifluoride, the lithio compound (4c) was obtained from 3-bromo-4-methylbenzotrifluoride (3c), which was then converted to [2-methyl-5-(trifluoromethyl)phenyl]acetylene (1c) (43% overall yield). The bromide (3c) was prepared in 52% yield by the fluorination of 3-bromo-4-methylbenzoic acid (8) with sulfur tetrafluoride (Scheme 2). Reaction of 4-methylbenzotrifluoride and bromine did not give the bromide (3c) but a large quantity of benzoic acid derivatives as by-products due to hydrolysis of the trifluoromethyl group.

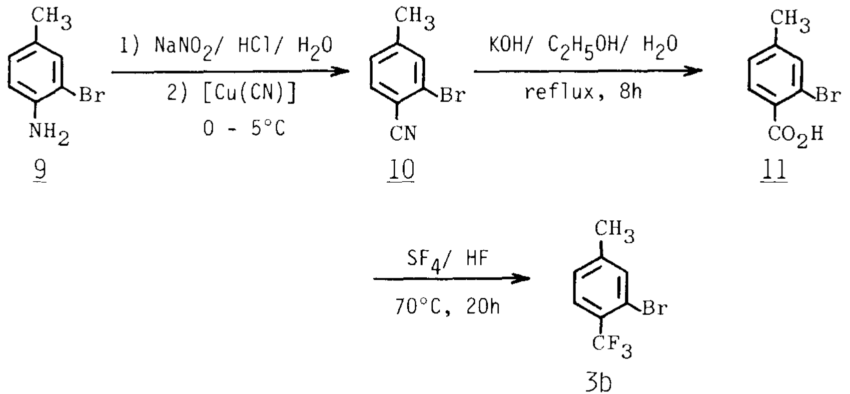


Scheme 2

[5-Methyl-2-(trifluoromethyl)phenyl]acetylene (1b) was prepared in 50% overall yield from 2-bromo-4-methylbenzotrifluoride (3b), and 3b was prepared as shown in Scheme 3. Preparation of 2-bromo-4-methylbenzonitrile (10) was carried out by Sandmeyer reaction from 2-bromo-p-toluidine (9), and the carboxylic acid (11) was obtained by the hydrolysis of 10.

The fluorination of 11 with sulfur tetrafluoride provided the benzotrifluoride (3b) in 79% yield.

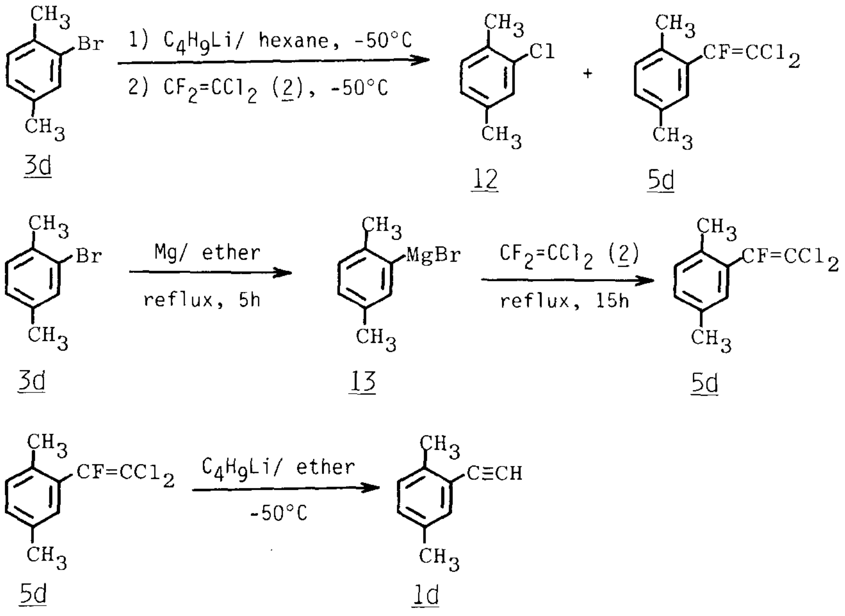
As the fluorination of *p*-toluic acid with sulfur tetrafluoride at 130°C gave 4-methylbenzotrifluoride in high yield, we attempted the fluorination of bromo(methyl)benzoic acids (8 and 11) under similar conditions, but only a tarry product resulted. By lowering the reaction temperature (70°C), however, 3b and 3c were obtained in moderate yields.



Scheme 3

The reaction between the bromides (3b,c) and butyllithium provided the lithio compounds (4b,c). The reaction of these lithio compounds (4) with $CF_2=CCl_2$ (2) had to be run by the inverse addition method in order to prevent the formation of chloro(methyl)benzotrifluorides caused by the Cl-Li exchange. In the case of 2-bromo-*p*-xylene (3d), neither method of addition could prevent the Cl-Li exchange, forming predominantly 2-chloro-*p*-xylene (5d : 12 = 1 : 3) (Scheme 4).

The results are in agreement with Okuhara's proposal that the main determining factor of the proportion of the exchange is the extent of delocalization of the negative charge in the reagent [7]. Therefore, (2,5-dimethylphenyl)acetylene (1d) was prepared by the procedure using the Grignard reagent (13) (28% overall yield) (Scheme 4). As we have shown, the electronegativity of the substituents significantly affected the formation of the lithio compounds (4), but their positions hardly influenced the lithiation.



Scheme 4

Polymerization of 2,5-disubstituted phenylacetylenes

Polymerization of 2,5-disubstituted phenylacetylenes was accomplished in the following three ways [3-6].

A. $W(CO)_6$-CCl_4-light irradiation system

B. WCl_6-Ph_4Sn system

C. γ-ray induced polymerization

The reaction conditions, yields and molecular weights of the formed polymers are summarized in Tables I - III. The attempts of polymerization using $TaCl_5$ were unsuccessful.

For all four monomers, the polymerization using transition metal catalysts (methods A and B) offered high-molecular-weight polymers in high yields (above 90%), but the polymerization of 1a by method B was considered to give cross linked polymers because it only swelled and was insoluble in organic solvents such as THF. The molecular weights of polymers obtained were found to increase by introduction of trifluoromethyl groups. However, the polymerization of the acetylenes having both trifluoromethyl and methyl groups (1b and 1c), provided larger molecular weight polymers than the acetylene having only trifluoromethyl groups (1a) (the molecular weights decreased in the following order, poly(1c) >poly(1b)>poly(1a)>poly(1d)). The earlier papers have suggested that the polymerizability of phenylacetylene is improved when the substituent possesses high electronegativity [3] and steric hindrance [4]. In spite of having the most electronegative and bulky substituents, the polymerization of 1a did not always offer the highest molecular weight polymer.

TABLE I

Polymerization by $W(CO)_6$-CCl_4-hν (A)[a].

Monomer	$[M]_0$ mol/l	$W(CO)_6$ mmol/l	Yield (%)	$\overline{Mw}$[b] ($x10^4$)	$\overline{Mn}$[b] ($x10^4$)
1a	0.20	56.8	92	11.4	8.4
1b	0.22	56.8	92	17.3	11.9
1c	0.22	56.8	100	45.6	29.1
1d	0.30	56.8	95	6.0	2.2

[a] Polymerized in carbon tetrachloride at 30°C for 24h.
[b] Determined by GPC.

TABLE II

Polymerization by WCl_6-Ph_4Sn (B)[a].

Monomer	$[M]_0$ mol/l	WCl_6 mmol/l	Ph_4Sn mmol/l	Yield (%)	$\overline{Mw}$[b] ($x10^4$)	$\overline{Mn}$[b] ($x10^4$)
1a	0.68	10	10	96[c]	-	-
1b	0.75	10	10	67	14.4	9.7
1c	0.73	10	10	100	16.7	9.3
1d	0.70	10	10	100	5.4	2.9

[a] Polymerized in toluene at 30°C for 24h. [b] Determined by GPC. [c] Totally insoluble in THF.

TABLE III

γ-Ray Induced Polymerization (C)[a]

Monomer	Yield (%)	$\overline{Mw}$[b] ($\times10^4$)	$\overline{Mn}$[b] ($\times10^4$)
1a	87[c]	50.1	45.2
1b	27	2.6	1.3
1c	12	1.1	0.6
1d	5	0.3	0.2

[a] Polymerized by γ-ray (Co^{60} 38 Mrad) at ambient temperature.

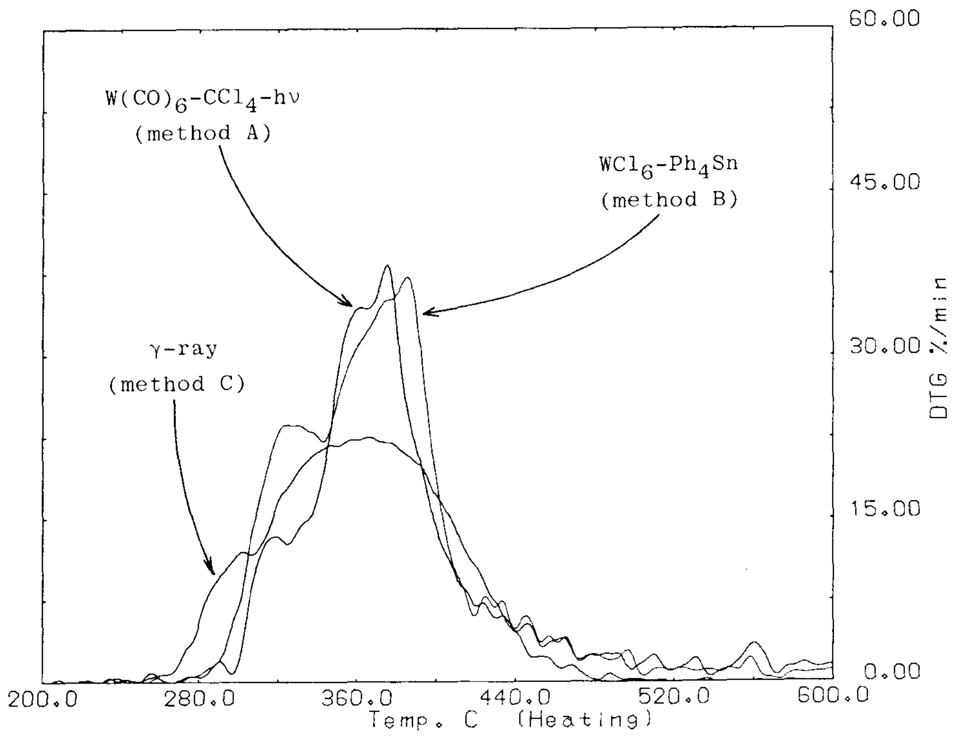
[b] Determined by GPC. [c] Partly insoluble in THF.

As the phase separation of the polymerization mixture occurred in the course of the polymerization because of low solubilities of the polymers, the propagation of the polymerization might be suppressed. This result indicates that the solubility of polymer also affects its molecular weight.

The γ-ray induced polymerization (method C) demonstrated a positive correlation between the yields and molecular weights of obtained polymers. Both of them increased with increasing number of trifluoromethyl groups (poly(1a)>poly(1b)>poly(1c) >poly(1d)). The majority of the polymer from 1a was insoluble in THF. The γ-ray induced polymerization was less effective for the polymerization of other phenylacetylene (1b-d) and unreacted monomers were mostly recovered. The tendency of polymerization is considered to be due to the efficiency of the irradiation energy of γ-rays. Probably, the electron attraction of trifluoromethyl groups shifts π-electron energy levels of ethynyl groups to lower levels.

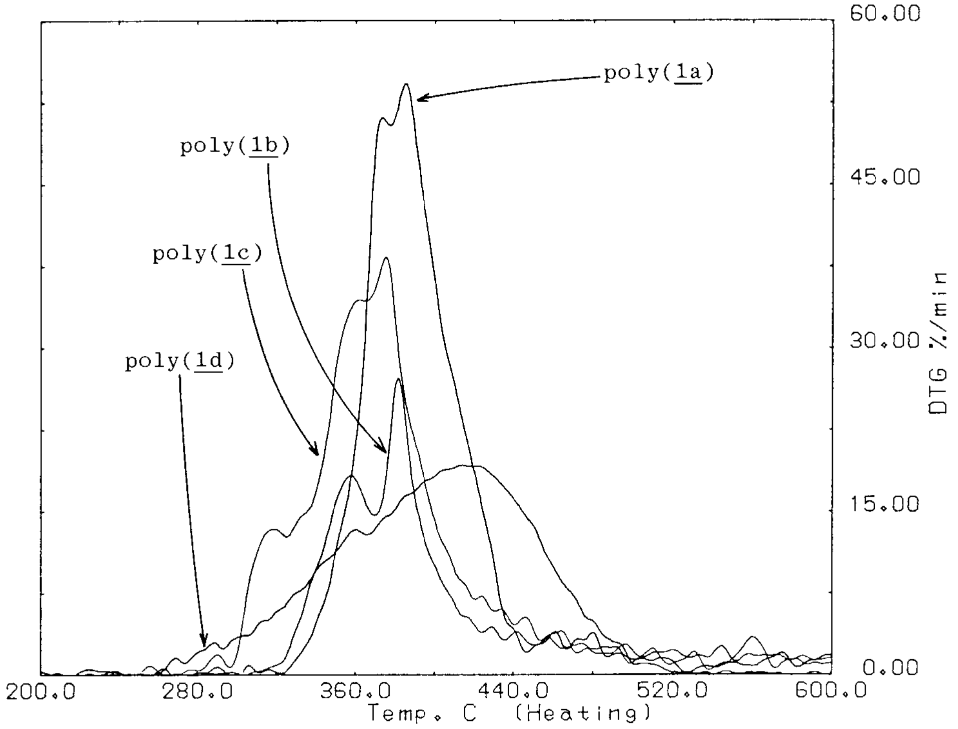
Thermogravimetric analyses of the polymers

The initiation points of thermal decomposition (Td) of polymers obtained are indicated in Table IV, and the differential curves of weight loss (DTG curve) are shown in Figs. 1 and 2.



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

Fig. 1. Thermogravimetric analysis of poly(<u>1c</u>) made by various polymerization methods. (the differential curves of Tg).



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

Fig.2. Thermogravimetric analysis of poly(2,5-disubstituted acetylene) made by $W(CO)_6$-CCl_4-hν system (method A). (the differential curves of Tg).

TABLE IV

Thermal Decomposition Points of Polymers (°C).

Polymer	$W(CO)_6$-CCl_4 (A)	WCl_6-Ph_4Sn (B)	γ-ray (C)
poly(<u>1a</u>)	327	334	311
poly(<u>1b</u>)	311	308	300
poly(<u>1c</u>)	297	281	265
poly(<u>1d</u>)	260	260	224

In the case of polymers obtained by methods A and B, Td values were approximately equal, but slightly higher than those by method C (Fig.1). This is because γ-ray induced polymerization (method C) produced polymers having more branches than those by methods A and B. Independent of polymerization methods, Td values increased with increasing number of trifluoromethyl groups. The presence of trifluoromethyl groups at the <u>ortho</u>-position to the ethynyl group especially raised Td (Fig.2, poly(<u>1c</u>) and poly(<u>1b</u>)). Hence, Td values seemed to be influenced by both the electron attraction and steric hindrance of the trifluoromethyl group.

It has been proposed that the thermal degradation of the polyacetylenes involves the process of formation of biradicals, and the twisted conformation of the main chain obstructs the production of biradicals [9]. The <u>ortho</u>-position substituent of a polyphenylacetylene should much more affect the conformation of the main chain in the polymer than substituents in other positions. Therefore, introduction of the trifluoromethyl group at the <u>ortho</u>-position relative to the ethynyl group is considered to enhance the Td value of the polymer.

EXPERIMENTAL

All melting and boiling points are uncorrected. The reactions using n-butyllithium or the transition metal compounds such as WCl_6 were carried out under argon atmosphere.

Instruments

IR spectra were recorded on a JASCO IR-810 infrared spectrophotometer. ^1H NMR (90MHz) and ^{19}F NMR (84.67MHz) measurements were performed in $CDCl_3$ on a Hitachi R-90H instrument, and the chemical shifts are defined as the δ values referenced to TMS (internal) or CF_3CO_2H (external) respectively. Mass spectra and GC-Mass spectra were obtained on a Hitachi M-80 instrument (electron-impact ionization at 20eV). Elemental analyses were recorded on a Perkin-Elmer 240B analyzer. The molecular weights of polymers were determined by gel permeation chromatography (GPC) using a polystyrene calibration. The GPC was measured by a Jasco Trirotar liquid chromatograph (eluent:THF ; column Shodex A80M). Thermal gravity analyses were performed on a Seiko I & E SSC/580 II instrument.

Reagents

A solution of n-butyllithium was prepared from butylbromide and lithium metal in anhydrous ether. 1,1-Dichloro-2,2-difluoroethylene (2) was prepared by the reported method [7]. [2,5-Bis(trifluoromethyl)phenyl]acetylene (1a) was prepared according to the previous paper [8]. Other reagents were all commercially obtained, and used without further purification.

3-Bromo-4-methylbenzoic acid (8)

To a mixture of ethyl 4-methylbenzoate (6) (61.1g, 0.372mol) and iron powder (1.20g, 0.022g-atom) in CCl_4 (100ml), was added a solution of bromine (63.3g, 0.408mol) in CCl_4 (43ml), and then stirring was continued for 3h at 70-75°C. The reaction mixture was cooled and poured into a $NaHSO_3$ solution. The organic layer was separated and evaporated. To the residue, was added an aqueous 10% NaOH solution (200ml), which was refluxed for 3h. After cooling, the solid material was filtered off, and the filtrate was acidified with conc. HCl. Formed precipitates were collected and recrystallized from ethanol to yield 3-bromo-4-methylbenzoic acid (8) (34.6g, 43%) : mp. 204-206°C (lit. 203-204°C [10]); MS m/e (relative intensity), 216,214 (100) M^+, 199,197 (33) $[M - OH]^+$, 171,169 (29) $[M - CO_2H]^+$, 135 (25) $[M - Br]^+$.

2-Bromo-4-methylbenzonitrile (10)

To a suspension of 2-bromo-4-methylaniline (9) (51.4g, 0.276mol) in 5N HCl (150ml), was added with stirring an aqueous solution of $NaNO_2$ (14.2g, 0.203mol) at 0-5°C, and stirring was continued for 2h. The reaction mixture was neutralized with Na_2CO_3, and then was added a suspension of copper cyanide (83.3g, 0.522mol) in water (70ml) and toluene (200ml) at 0-5°C. The reaction mixture was stirred for 30min further, and then for an additional 2h at room temperature. The toluene layer was separated, and was then steam distilled. After removal of toluene, the residual material was recrystallized from ethanol to yield 2-bromo-4-methylbenzonitrile (10) (26.0g, 48%): IR (nujol), 2205($\nu C{\equiv}N$), 1600, 1490, 1270, 1200, 1050, 1040, 950, 890, 860, 810cm^{-1}.

2-Bromo-4-methylbenzoic acid (11)

A solution of 2-bromo-4-methylbenzonitrile (10) (22.5g, 0.115mol) in 150ml of ethanol was added to an aqueous solution (50ml) of KOH (9.05g, 0.115mol), and was heated under refluxing for 8h. The reaction mixture was evaporated, and the residual aqueous solution was acidified with conc. HCl. The resultant white precipitate was collected. 2-Bromo-4-methylbenzoic acid (11) (19.9g, 81%) was obtained by recrystallization from water-ethanol(2:5) : mp. 141°C (lit. 141-142°C [11]); MS m/e (relative intensity), 216,214 (86) M+, 199,197 (100) $[M - OH]^+$, 171,169 (20) $[M - CO_2H]^+$, 135 (3) $[M - Br]^+$.

3-Bromo-4-methylbenzotrifluoride (3c)

In a 100ml autoclave made of Hastelloy C, was placed a mixture of 3-bromo-4-methylbenzoic acid (8) (20.0g, 0.093mol) and anhydrous hydrogen fluoride (20ml). The autoclave was cooled with liquid nitrogen, and sulfur tetrafluoride (45.5g, 0.421mol) was added using a vacuum line. Then the autoclave was heated at 70°C for 20h. After cooling the autoclave with water, the contents were poured into ice-water and extracted with ether, and the extract was washed with an aqueous 10% KOH solution. The ether solution was dried over anhydrous Na_2SO_4, and evaporated. The residue was distilled to give 3-bromo-4-methylbenzotrifluoride (3c) (23.3g, 52%).

(3c): bp. 66-67°C(20mmHg); MS m/e (relative intensity), 240,238 (86) M^+, 221,219 (11) $[M - F]^+$, 171,169 (15) $[M - CF_3]^+$, 159 (100) $[M - Br]^+$; ^{1}H-NMR, 7.76 (s,1H), 7.39-7.22(AB,2H), 2.42 (s,CH_3) (lit. 7.5(m,3H), 2.35(s,3H) [12]); ^{19}F-NMR, 16.00(s,CF_3); Elemental analysis, Found C,39.92%, H,2.47%, Calcd. as $C_8H_6F_3Br$, C,40.20%, H,2.53%.

2-Bromo-4-methylbenzotrifluoride (3b)

By a similar procedure to 3c, 2-bromo-4-methylbenzotrifluoride (3b) was obtained in 79% yield from 11.

(3b): nc; bp. 80°C(20mmHg); MS m/e (relative intensity), 240,238 (100) M^+, 221,219 (10) $[M - F]^+$, 171,169 (40) $[M - CF_3]^+$, 159 (58) $[M - Br]^+$; ^{1}H-NMR, 7.56-7.10(AB,2H), 7.48(s,1H), 2.34(s,CH_3); ^{19}F-NMR, 16.46(s,CF_3); Elemental analysis, Found C,40.26%, H,2.36%, Calcd. as $C_8H_6F_3Br$, C,40.20%, H,2.53%.

1-Methyl-4-trifluoromethyl-2-(2',2'-dichloro-1'-fluorovinyl) benzene (5c)

To a solution of 3-bromo-4-methylbenzotrifluoride (3c) (18.9 g, 0.079mol) in anhydrous diethyl ether (50ml), cooled at -50°C, was added ethereal n-butyllithium (73ml, 0.116mol). After stirring for 30 min, the reaction mixture was dropped into a solution of $CF_2=CCl_2$ (2) (31.5g, 0.237mol) in anhydrous ether (30ml) by the inverse addition method, keeping the reaction temperature below -50°C. The reaction mixture was stirred for an additional 30 min, and then poured into a mixture of conc. HCl and crushed ice. The ether layer was separated, dried and then the solvent was evaporated. The residue was vacuum distilled to yield 5c (13.1g, 61%).

(5c): nc; bp. 96°C(15mmHg); MS m/e (relative intensity), 276,274,272 (49) M^+, 239,237 (33) $[M - Cl]^+$, 202 (19) [M -

2Cl]$^+$, 201 (100) [M - H - 2Cl]$^+$, 133 (34); ^{1}H-NMR, 7.66 (s,1H), 7.57-7.24(AB,2H), 2.42(s,CH_3); ^{19}F-NMR, 16.11(s,CF_3), -10.34(s,F); Elemental analysis, Found C,44.13%, H,2.03%, Calcd. as $C_{10}H_6F_4Cl_2$ C,43.99%, H,2.21%.

[2-Methyl-5-(trifluoromethyl)phenyl]acetylene (1c)

To a solution of 5c (10.2g, 0.020mol) in anhydrous diethyl ether (40ml), ethereal n-butyllithium (55ml, 0.086mol) was added and stirred for 30 min at -50°C. The reaction mixture was poured into a mixture of conc. HCl and crushed ice. The ether layer was separated, washed with $NaHCO_3$ solution and water. The ether layer was dried over Na_2SO_4, and was distilled to yield 1c (4.87g, 71%).

(1c): nc; bp. 71°C(20mmHg); MS m/e (relative intensity), 184 (100) M$^+$, 115 (89) [M - CF_3]$^+$; ^{1}H-NMR, 7.69(s,1H), 7.40-7.22(AB,2H), 3.31(s,C≡CH), 2.47(s,CH_3); ^{19}F-NMR, 15.85(s,CF_3); Elemental analysis, Found C,64.98%, H,3.53%, Calcd. as $C_{10}H_7F_3$ C,65.22%, H,3.83%.

1-Methyl-4-trifluoromethyl-3-(2',2'-dichloro-1'-fluorovinyl) benzene (5b)

By a similar procedure to 5c, 5b was obtained in 71% yield from 4b.

(5b): nc; bp. 107-108°C(27mmHg), MS m/e (relative intensity), 276,274,272 (100) M$^+$, 239,237 (86) [M - Cl]$^+$, 202 (17) [M - 2Cl]$^+$, 201 (17) [M - H - 2Cl]$^+$; ^{1}H-NMR, 7.69-7.23(AB,2H), 7.35(s,1H), 2.43(s,CH_3); ^{19}F-NMR, 17.30(d,CF_3), -6.21(q,F); Elemental analysis, Found C,44.19%, H,2.13%, Calcd. as $C_{10}H_6F_4Cl_2$ C,43.99%, H,2.21%.

[5-methyl-2-(trifluoromethyl)phenyl]acetylene (1b)

By a similar procedure to 1c, 1b was obtained in 70% yield from 5b.

(1b): nc; bp. 80°C(20mmHg), MS m/e (relative intensity), 184 (52) M$^+$, 115 (100) [M - CF_3]$^+$; 7.54-7.12(AB,2H), 7.41(s,1H), 3.29(s,C≡CH), 2.32(s,CH_3); ^{19}F-NMR, 16.79(s,CF_3); Elemental analysis, Found C,65.03%, H,3.64%, Calcd. as $C_{10}H_7F_3$ C,65.22%, H,3.83%.

1,4-Dimethyl-2-(2',2'-dichloro-1'-fluorovinyl)benzene (5d)

(1) via lithio compound

To a solution of 2-bromo-p-xylene (3d) (30.2g, 0.163mol) in anhydrous diethyl ether (180ml), was added ethereal n-butyllithium (142ml, 0.228mol) at -40 to -50°C. The temperature of the reaction mixture was allowed to rise to 0°C. After stirring for 1h, the reaction suspension was added to a solution of $CF_2=CCl_2$ (2) (65.0g, 0.489mol) in anhydrous ether (100ml). After confirmation of complete consumption of the starting material by means of GC analysis, the reaction mixture was poured into an aqueous HCl solution. The ether layer was separated, washed with aqueous $NaHCO_3$ solution and water. GC-Mass analysis of the ether layer showed two products, 5d and 12, from which 12 was removed by fractional distillation. There was obtained 3.3g (9% yield) of 5d.

(2) via Grignard reagent

To magnesium ribbons (2.73g, 0.112g-atom), was added anhydrous diethyl ether (20ml) with gently stirring by a mechanical stirrer. A small amount of 2-bromo-p-xylene diluted in anhydrous ether was added in order to initiate the reaction, and the remainder of the diluted bromide was then added dropwise to maintain refluxing (total amount of bromide: 18.9g, 0.102mol). After stirring for 2h under refluxing, the reaction mixture was poured into an aqueous HCl solution, and was worked up as mentioned above to give 5d (8.69g, 39%).
(5d): nc; bp. 99°C(10mmHg) ; MS m/e (relative intensity), 220,218 (60) M^+, 185,183 (49) $[M - Cl]^+$, 147 (100) $[M - H - 2Cl]^+$, 133 (26) $[M - Cl - CH_3]^+$; ^{1}H-NMR, 7.15(s,1H), 7.11 (s,2H), 2.28(s,CH_3), 2.18(s,CH_3'); ^{19}F-NMR, -8.32(s,F); Elemental analysis, Found C,55.01%, H,4.13%, Calcd. as $C_{10}H_9FCl_2$ C,54.82%, H,4.14%.
(12): MS m/e (relative intensity), 142,140 (58) M^+, 105 (100) $[M - Cl]^+$.

(2,5-Dimethylphenyl)acetylene (1d)

By a similar procedure to 1c, there was obtained 1d in 71% yield from 5d.

(1d): bp. 90°C(30mmHg) (lit.49°C(2mmHg) [13]); MS m/e (relative intensity), 130 (88) M^+, 129 (44) $[M - H]^+$, 115 (100) $[M - CH_3]^+$; ^{1}H-NMR, 7.255 (s,1H), 7.03(s,2H), 3.19(s,C≡CH), 2.38(s,CH_3), 2.25(s,CH_3'); Elemental analysis, Found C,92.48%, H,7.56%, Calcd. as $C_{10}H_{10}$ C,92.26%, H,7.74%.

Polymerization of 2,5-disubstituted phenylacetylenes

(1) by $W(CO)_6$-CCl_4-light irradiation system (method A)

A solution of $W(CO)_6$ (0.50g, 1.4mmol) in carbon tetrachloride (25ml) was activated by irradiating with a 100 watt high-pressure-mercury lamp at 30°C for 30min. A monomer acetylene (1.00g) was added to this catalytic solution, and continued to react in a dark place at 30°C for 24h. The polymerization was terminated with methanol, and the precipitated polymers were purified by dissolving in THF and reprecipitating with methanol. The polymers were collected by filtration, washed with methanol, and dried to constant weight.

(2) by WCl_6-Ph_4Sn system (method B)

In a three-necked flask were placed WCl_6 (21mg) and Ph_4Sn (23mg) dissolved in toluene (5ml) and stirred for 30min. The catalytic solution was added to monomer (0.7g) in another flask. After polymerization at 30°C for 24h, the reaction was terminated by addition of methanol. Formed precipitates were collected, then washed with methanol and dried to constant weight.

(3) by $TaCl_5$ system

Polymerization was carried out according to a similar procedure to the method B.

(4) γ-ray induced polymerization (method C)

In an ampoule was placed the monomer (0.5ml), and degassed by a successive freezing and melting procedure. The ampoule was sealed under vacuum, and was irradiated by the γ-ray (^{60}Co) of 3.34×10^5 rad/h for 114h at ambient temperature without any solvents. The contents of the ampoule were poured into methanol, and the precipitate formed was collected by filtration, and washed by methanol and dried to constant weight.

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