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**SYNTHESIS OF 1,4-BIS(p-ARYLOXY-TETRAFLUOROPHENYL)BUTADIYNE
MONOMERS FOR NONLINEAR OPTICS**

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SUMMARY

Novel diacetylenes with polyfluorophenyl groups directly bound to the diacetylene moiety, 1,4-bis(p-aryloxy-tetrafluorophenyl)butadiynes, were prepared in four steps from pentafluoriodobenzene and trimethylsilylacetylene.

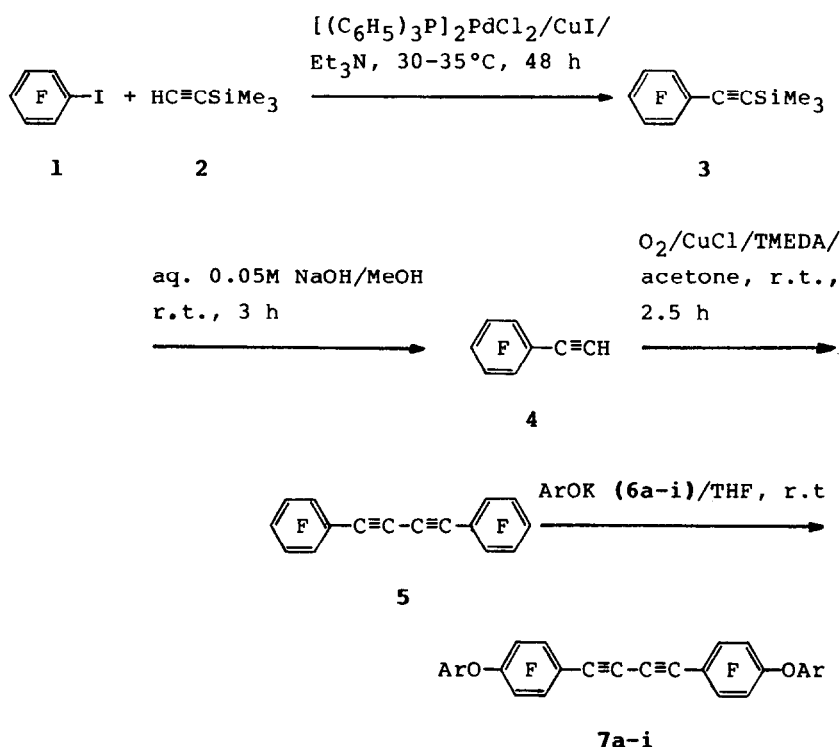
INTRODUCTION

The work of Wegner and co-workers has shown that the solid-state polymerization of diacetylenes $R-C\equiv C-C\equiv C-R'$ can yield large, defect-free, single crystalline and one-dimensional fully conjugated polydiacetylenes of the type $[C(R)-C\equiv C-(R')C=]$ [1-4]. The reactivity of polymerization is mainly controlled by the monomer crystal packing [3,4]. Nonlinear optical properties of polydiacetylenes have received considerable attention recently due to their demonstrated large third-order nonlinearities and potential application in the area of integrated optics [5-8]. Up to now quite a large number of symmetrical diacetylene monomers with methylene groups next to the diacetylene moiety have been prepared for nonlinear optics [4,6]. To achieve higher third-order nonlinearity, diacetylene mono-

mers with more π -electrons might be good candidates [9]. In this paper, we describe the synthesis of 1,4-bis(p-aryloxy-tetrafluorophenyl)butadiynes which are the monomers of poly-[1,4-bis(p-aryloxy-tetrafluorophenyl)butadiynes] used as nonlinear optical materials. The polymerization and nonlinear properties of these diacetylenes are now under study.

RESULTS AND DISCUSSION

1,4-Bis(p-aryloxy-tetrafluorophenyl)butadiynes (**7a-i**) were prepared via the following procedure.

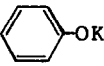
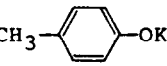
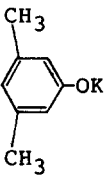
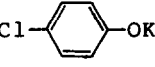
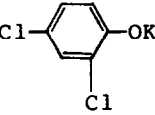
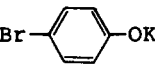
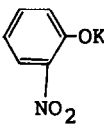
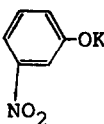
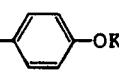


TMEDA = $(CH_3)_2NCH_2CH_2N(CH_3)_2$

Scheme 1.

TABLE 1

Preparation of 1,4-Bis(p-aryloxy-tetrafluorophenyl)butadiynes (7a-i) from 1,4-Bis(pentafluorophenyl)butadiyne (5)

No	ArOK 6a-i	Reaction conditions solvent/temp./time	Product 7a-i		
			No	Yield ^a (%)	M.p. ^b (°C)
6a		THF/r.t./15 min	7a	85	186
6b		THF/r.t./15 min	7b	78	193
6c		THF/r.t./15 min	7c	75	171
6d		THF/r.t./25 min	7d	88	195
6e		THF/r.t./6 h	7e	74	138
6f		THF/r.t./30 min	7f	84	196
6g		THF/45°C/1 h	7g	73	240
6h		THF/r.t./1 h	7h	90	221
6i		THF/r.t./45 min	7i	86	236

^a Isolated yield.

^b Not corrected.

Previously we have reported the palladium-catalyzed coupling reaction between pentafluoriodobenzene (**1**) and trimethylsilylacetylene (**2**) [10] to give [(pentafluorophenyl)ethynyl]trimethylsilane (**3**) which yielded (pentafluorophenyl)ethyne (**4**) after removal of the trimethylsilyl group with sodium hydroxide in methanol at ambient temperature. 1,4-Bis(pentafluorophenyl)butadiyne (**5**) [11] was prepared from (**4**) in high yield by the method of Hay [12]. Nucleophilic substitutions on [(pentafluorophenyl)ethynyl]trimethylsilane give para-substituted products [13]. 1,4-bis(pentafluorophenyl)butadiyne (**5**) reacted with corresponding aroxides, ArOK (**6a-i**) to give 1,4-bis(p-aryloxy-tetrafluorophenyl)butadiynes (**7a-i**) in good yields.

We found that **7a**, **7b**, **7c**, **7e** and **7f** (substituents as shown in Table 1) turned violet or red upon exposure to heat and light to give insoluble polydiacetylenes, $[C(R)-C\equiv C-(R)C]_n$. It is well known that diphenyldiacetylene and dicarbazolyldiacetylene having aromatic rings directly bound to the diacetylene moiety are not polymerizable in the solid-state [14], and several substituted diphenyldiacetylenes give polydiacetylenes only in low conversion [15,16]. It is noteworthy that we found that diacetylenes with fluoro-aromatic rings directly bound to the diacetylene moiety have reactivities towards solid-state polymerization. Exposed to $\lambda = 5154 \text{ \AA}$ laser, polymerizable fluoro-diacetylenes, **7a**, **7b**, **7c**, **7e**, **7f** and also 5 partially polymerized to yield one or several new C $\equiv$ C bonds [17] as shown in the EXPERIMENTAL PART.

EXPERIMENTAL

IR spectra were recorded on a Shimadzu IR-440 spectrometer. Raman spectra were recorded on a JY-T 800 spectrometer. ^1H NMR spectra were recorded on a Varian EM 360A (60 MHz) instrument. ^{19}F NMR spectra were recorded on a Varian EM 360L (60 MHz) instrument (high field is positive). MS spectra were recorded on a Finnigan-4021 spectrometer.

[(Pentafluorophenyl)ethynyl]trimethylsilane (**3**) was prepared by the method reported previously [10].

(Pentafluorophenyl)ethyne (**4**): To a solution of [(pentafluorophenyl)ethynyl]trimethylsilane (**3**; 14.5 g, 54.9 mmol) in methanol was added aqueous sodium hydroxide (0.05 M, 20 ml) at room temperature with stirring. After 3 h, the mixture was acidified with dilute hydrochloric acid and extracted with ether, and then dried with Na_2SO_4 . The solvent was removed and the residue was distilled to give (pentafluorophenyl)acetylene (**4**) 7.2 g (69%); b.p. 53–54°C/mmHg (Ref. [18] b.p. 130–131°C). IR (neat); $\nu = 3300, 2132, 1520, 1500 \text{ cm}^{-1}$. ^1H NMR (CCl_4/TMS): $\delta = 3.47$ (s, $\text{C}\equiv\text{C-H}$) ppm. ^{19}F NMR ($\text{CCl}_4/\text{CF}_3\text{COOH}$): $\delta = 59.71$ (m, 2 F, F_{arom}), 75.80 (t, 1 F, F_{arom}), 85.72 (m, 2 F, F_{arom}) ppm.

1,4-Bis(pentafluorophenyl)butadiyne (**5**) [12]: Cuprous chloride (0.5 g), N, N, N', N'-tetramethylethylenediamine (1.2 ml) and acetone (150 ml) were placed in a four-necked flask at room temperature. Oxygen was bubbled through the solution via a tube, and the mixture was stirred vigorously. (Pentafluorophenyl)ethyne (**4**; 5.8 g, 30 mmol) in acetone (30 ml) was added within 30 min. After 3.5 h, the acetone was removed and then dilute hydrochloric acid (50 ml, $\text{HCl}/\text{H}_2\text{O} = 1:10$) was added. The solid was recrystallized from acetone-water to give 1,4-bis-(pentafluorophenyl)butadiyne (**5**) as white crystals 5.2g (90%); m.p. 114–115°C. IR(KBr): $\nu = 1515, 1500, 1432 \text{ cm}^{-1}$. Raman (neat): $\nu = 2233$ ($\text{C}\equiv\text{C}$ of monomer), 2106 ($\text{C}\equiv\text{C}$ of polymer) cm^{-1} . ^{19}F NMR ($\text{CCl}_4/\text{CF}_3\text{COOH}$): $\delta = 57.32$ (m, 4F, F_{arom}), 71.20 (t, 2F, F_{arom}), 83.23 (m, 4 F, F_{arom}) ppm; MS m/z : 382 (M^+). Analysis Found: C, 50.47%; F, 50.03%. $\text{C}_{16}\text{F}_{10}$ Calc.: C, 50.26%; F, 49.74%.

Compounds **7a-i** were new.

1,4-Bis[p-(4-chloro-phenoxy)-tetrafluorophenyl]butadiyne(**7d**)
Typical procedure: To a solution of 1,4-(pentafluorophenyl)-butadiyne (**5**; 100 mg, 0.26 mmol) in THF (2 ml) was added p-Cl- $\text{C}_6\text{H}_4\text{-OK}$ (**6d**; 150 mg, 0.9 mmol) at room temperature with stirring for 25 min. Then the mixture was diluted with water (10ml)

, a yellow solid appeared. The pale yellow product was recrystallized from acetone-water to give (7d) as colorless crystals; 138mg (88%), m.p. 195°C. IR (KBr): ν = 1596, 1500, 1485, 1428 cm^{-1} . Raman (neat): ν = 2223 cm^{-1} . ^1H NMR (CDCl_3/TMS): δ = 6.92 (d, 4 H, H_{arom} , J = 8.3 Hz), 7.38 (d, 4 H, H_{arom} , J = 8.3 Hz) ppm. ^{19}F NMR ($\text{CDCl}_3/\text{CF}_3\text{COOH}$): δ = 57.23 (m, 4 F, F_{arom}), 75.88 (m, 4 F, F_{arom}) ppm. MS m/z: 599 (M^+). Analysis Found: C, 56.18%; H, 1.04%; F, 25.34%; Cl, 11.56%. $\text{C}_{28}\text{H}_8\text{Cl}_2\text{F}_8\text{O}_2$ Calc. C, 56.09%; H, 1.34%; F, 25.38%; Cl, 11.85%.

The following compounds were prepared similarly.

1,4-Bis(p-phenoxy-tetrafluorophenyl)butadiyne (7a): m.p. 186°C. IR (KBr): ν = 1500, 1490, 1425 cm^{-1} . Raman (neat): ν = 2222 ($\text{C}\equiv\text{C}$ of monomer), 2099 ($\text{C}\equiv\text{C}$ of polymer) cm^{-1} . ^1H NMR (CCl_4/TMS): δ = 7.05-7.70 (m, H_{arom}) ppm. ^{19}F NMR ($\text{CCl}_4/\text{CF}_3\text{COOH}$): δ = 56.72 (m, 4 F, F_{arom}), 75.08 (m, 4 F, F_{arom}) ppm. MS m/z: 530 (M^+). Analysis Found: C, 63.60%; H, 1.69%; F, 28.89%. $\text{C}_{28}\text{H}_{10}\text{F}_8\text{O}_2$ Calc.: C, 63.40%; H, 1.89%; F, 28.68%.

1,4-Bis[p-(4-methyl-phenoxy)-tetrafluorophenyl]butadiyne (7b): m.p. 193°C. IR (KBr): ν = 1500, 1490, 1423 cm^{-1} . Raman (neat): ν = 2223 ($\text{C}\equiv\text{C}$ of monomer), 2106 ($\text{C}\equiv\text{C}$ of polymer) cm^{-1} . ^1H NMR (CCl_4/TMS): δ = 2.33 (s, 6H, $2\times\text{CH}_3$), 6.87 (d, 4 H, H_{arom} , J = 8.5 Hz), 7.15 (d, 4 H, H_{arom} , J = 8.5 Hz) ppm. ^{19}F NMR ($\text{CCl}_4/\text{CF}_3\text{COOH}$): δ = 57.45 (m, 4 F, F_{arom}), 75.68 (m, 4 F, F_{arom}) ppm. MS m/z: 558 (M^+). Analysis Found: C, 64.70%; H, 2.59%; F, 26.92%. $\text{C}_{30}\text{H}_{14}\text{F}_8\text{O}_2$ Calc.: C, 64.52%; H, 2.51%; F, 25.94%.

1,4-Bis[p-(3,5-dimethyl-phenoxy)-tetrafluorophenyl]butadiyne (7c): m.p. 171°C. IR (KBr): ν = 1500, 1485, 1423 cm^{-1} . Raman (neat): ν = 2221 ($\text{C}\equiv\text{C}$ of monomer), 2119, 2085 ($\text{C}\equiv\text{C}$ of polymer) cm^{-1} . ^1H NMR (CDCl_3/TMS): δ = 2.28 (s, 12 H, $4\times\text{CH}_3$), 6.56 (m, 6 H, H_{arom}) ppm. ^{19}F NMR ($\text{CDCl}_3/\text{CF}_3\text{COOH}$): δ = 57.33 (m, 4 F, F_{arom}), 75.50 (m, 4 F, F_{arom}) ppm. MS m/z: 586 (M^+). Analysis Found: C, 65.25%; H, 2.88%; F, 25.97%; $\text{C}_{32}\text{H}_{18}\text{F}_8\text{O}_2$ Calc. C, 65.53%; H, 3.07%; F, 25.94%.

1,4-Bis[p-(2,4-dichloro-phenoxy)-tetrafluorophenyl]butadiyne (7e): m.p. 138°C. IR (KBr): $\nu = 1587, 1495, 1478, 1430 \text{ cm}^{-1}$. Raman (neat): $\nu = 2115, 2080, 2075 \text{ (C}\equiv\text{C of polymer) cm}^{-1}$. $^1\text{H NMR (CDCl}_3\text{/TMS)}$: $\delta = 7.18\text{--}7.83 \text{ (m, } H_{\text{arom}}) \text{ ppm}$. $^{19}\text{F NMR}$ $\delta = 57.33 \text{ (m, 4F, } F_{\text{arom}}), 76.74 \text{ (m, 4F, } F_{\text{arom}}) \text{ ppm}$. MS m/z: 668 (M^+). Analysis Found: C, 50.04%; H, 0.62%; F, 22.64%; Cl, 21.56%. $\text{C}_{28}\text{H}_6\text{Cl}_4\text{F}_8\text{O}_2$ Calc.: C, 50.30%; H, 0.90%; F, 22.75%; Cl, 21.26%.

1,4-Bis[p-(4-bromo-phenoxy)-tetrafluorophenyl]butadiyne (7f): m.p. 196°C. IR (KBr): $\nu = 1580, 1495, 1480, 1425 \text{ cm}^{-1}$. Raman (neat): $\nu = 2220 \text{ (C}\equiv\text{C of monomer), 2118, 2085, 2067 (C}\equiv\text{C of polymer) cm}^{-1}$. $^1\text{H NMR (CDCl}_3\text{/TMS)}$: $\delta = 6.67 \text{ (d, 4 H, } H_{\text{arom}}, J = 8.4 \text{ Hz), 7.21 (d, 4 H, } H_{\text{arom}}, J = 8.4 \text{ Hz) ppm}$. $^{19}\text{F NMR (CDCl}_3\text{/CF}_3\text{COOH)}$: $\delta = 57.25 \text{ (m, 4F, } F_{\text{arom}}), 76.15 \text{ (m, 4F, } F_{\text{arom}}) \text{ ppm}$. MS m/z: 688 (M^+). Analysis Found: C, 49.02%; H, 1.18%; F, 22.43%; Br, 23.16%. $\text{C}_{28}\text{H}_8\text{Br}_2\text{F}_8\text{O}_2$ Calc.: C, 48.84%; H, 1.16%; F, 22.09%; Br, 23.26%.

1,4-Bis[p-(2-nitro-phenoxy)-tetrafluorophenyl]butadiyne (7g): m.p. 240°C. IR (KBr): $\nu = 1583, 1493, 1469, 1420 \text{ cm}^{-1}$. Raman (neat): $\nu = 2225 \text{ cm}^{-1}$. $^1\text{H NMR (acetone-}d_6\text{/TMS)}$: $\delta = 7.00\text{--}8.00 \text{ (m, } H_{\text{arom}}) \text{ ppm}$. $^{19}\text{F NMR (acetone-}d_6\text{/CF}_3\text{COOH)}$: $\delta = 60.34 \text{ (m, 4F, } F_{\text{arom}}), 79.79 \text{ (m, 4F, } F_{\text{arom}}) \text{ ppm}$. MS m/z: 620 (M^+). Analysis Found: C, 54.10%; H, 1.08%; N, 4.29%; F, 24.99%. $\text{C}_{28}\text{H}_8\text{F}_8\text{N}_2\text{O}_6$ Calc.: C, 54.19%; H, 1.29%; N, 4.52%; F, 24.52%.

1,4-Bis[p-(3-nitro-phenoxy)-tetrafluorophenyl]butadiyne (7h): m.p. 221°C. IR (KBr): $\nu = 1580, 1490, 1482, 1422 \text{ cm}^{-1}$. Raman (neat): $\nu = 2221 \text{ cm}^{-1}$. $^1\text{H NMR (acetone-}d_6\text{/TMS)}$: $\delta = 7.34\text{--}7.44 \text{ (m, } H_{\text{arom}}) \text{ ppm}$. $^{19}\text{F NMR (acetone-}d_6\text{/CF}_3\text{COOH)}$: $\delta = 60.00 \text{ (m, 4F, } F_{\text{arom}}), 78.00 \text{ (m, 4F, } F_{\text{arom}}) \text{ ppm}$. MS m/z: 620 (M^+). Analysis Found: C, 53.97%; H, 1.05%; N, 4.36%; F, 24.44%. $\text{C}_{28}\text{H}_8\text{F}_8\text{N}_2\text{O}_6$ Calc.: C, 54.19%; H, 1.29%; N, 4.25%; F, 24.52%.

1,4-Bis[(4-formoyl-phenoxy)-tetrafluorophenyl]butadiyne (7i): m.p. 236°C. IR (KBr): $\nu = 1700, 1600, 1500, 1490, 1430 \text{ cm}^{-1}$. Raman (neat): $\nu = 2221 \text{ cm}^{-1}$. $^1\text{H NMR (DMSO-}d_6\text{/TMS)}$: $\delta =$

7.40 (d, 4 H, H_{arom} , $J = 8.0$ Hz), 7.93 (d, 4 H, H_{arom} , $J = 8.0$ Hz), 9.82 (s, 2 H, 2xCHO) ppm. ^{19}F NMR (DMSO- d_6 /CF $_3$ COOH): $\delta =$ 59.12 (m, 4 F, F_{arom}), 78.34 (m, 4 F, F_{arom}) ppm. MS m/z : 586 (M^+). Analysis Found: C, 61.38%; H, 1.42%; F, 26.12%. C $_{30}$ H $_{10}$ F $_8$ O $_4$ Calc.: C, 61.43%; H, 1.71%; F, 25.94%.

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