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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 pentafluoroiodobenzene and trimethylsilylacetylene.

INTRODUCTION

The work of Wegner and co-workers has shown that the solid-state polymerization of diacetylenes R-C≡C-C≡C-R' can yield large, defect-free, single crystalline and one-dimensional fully conjugated polydiacetylenes of the type [=C(R)-C≡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-

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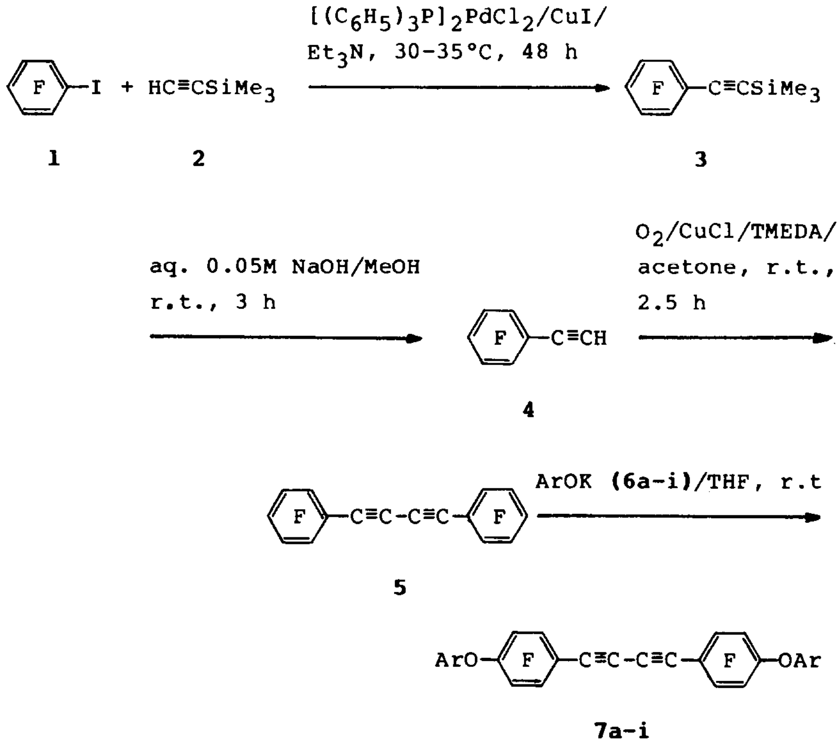
mers with more π-electrons might be good candidates [9]. In this paper, we describe the synthesis of 1,4-bis(p-aryloxy-tetrafluorophenyl)butadiynes which are the monomers of poly-[1,4-bis(p-aryloxy-tetrafluorophenyl)butadiynes] used as non-linear optical materials. The polymerization and nonlinear properties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

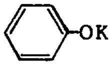
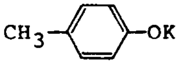
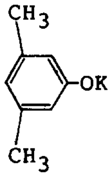
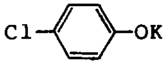
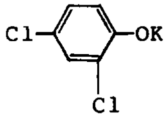
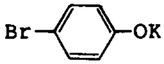
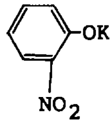
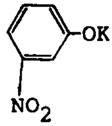
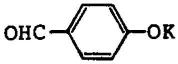


TMEDA = $(CH_3)_2NCH_2CH_2N(CH_3)_2$

Scheme 1.

TABLE 1

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

	ArOK	Reaction conditions	Product **7a-i**		
No	**6a-i**	solvent/temp./time	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 pentafluoroiodobenzene **(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 $\lambda = 5154$ Å 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].

<u>(Pentafluorophenyl)ethyne **(4)**</u>: 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); ν = 3300, 2132, 1520, 1500 cm^{-1}. ^1H NMR (CCl_4/TMS): δ = 3.47 (s, C≡C-H) ppm. ^{19}F NMR (CCl_4/CF_3COOH): δ = 59.71 (m, 2 F, F_{arom}), 75.80 (t, 1 F, F_{arom}), 85.72 (m, 2 F, F_{arom}) ppm.

<u>1,4-Bis(pentafluorophenyl)butadiyne **(5)** [12]</u>: 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, HCl/H_2O =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): ν=1515, 1500, 1432 cm^{-1}. Raman (neat) : ν=2233 (C≡C of monomer), 2106 (C≡C of polymer) cm^{-1}. ^{19}F NMR (CCl_4/CF_3COOH): δ = 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%. $C_{16}F_{10}$ Calc.: C, 50.26%; F,49.74%.

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

<u>1,4-Bis[p-(4-chloro-phenoxy)-tetrafluorophenyl]butadiyne**(7d)**</u>

Typical procedure: To a solution of 1,4-(pentafluorophenyl)butadiyne (**5**; 100 mg, 0.26 mmol) in THF (2 ml) was added p-Cl-C_6H_4-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 ($CDCl_3$/CF_3COOH): 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%. $C_{28}H_8Cl_2F_8O_2$ 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 (C≡C of monomer), 2099 (C≡C of polymer) cm^{-1}. ^1H NMR (CCl_4/TMS): δ =7.05-7.70(m,H_{arom}) ppm. ^{19}F NMR (CCl_4/CF_3COOH) : δ = 56.72 (m, 4 F, F_{arom}), 75.08 (m, 4F, F_{arom}) ppm. MS m/z : 530 (M^+). Analysis Found: C, 63.60%; H, 1.69%; F, 28.89%. $C_{28}H_{10}F_8O_2$ 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 (C≡C of monomer), 2106 (C≡C of polymer)cm^{-1}. ^1H NMR (CCl_4/TMS): δ = 2.33 (s, 6H, 2xCH_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 (CCl_4/CF_3COOH): 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%. $C_{30}H_{14}F_8O_2$ 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 (C≡C of monomer), 2119, 2085 (C≡C of polymer) cm^{-1}. ^1H NMR ($CDCl_3$/TMS): δ = 2.28 (s, 12 H, 4xCH_3) , 6.56 (m, 6 H, H_{arom}) ppm. ^{19}F NMR ($CDCl_3$/CF_3COOH): 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%; $C_{32}H_{18}F_8O_2$ 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): ν = 1587, 1495, 1478, 1430 cm^{-1}. Raman (neat): ν = 2115, 2080, 2075 (C≡C of polymer) cm^{-1}. ^{1}H NMR (CDCl$_3$/TMS): δ = 7.18-7.83 (m, Harom) ppm. ^{19}F NMR δ =57.33 (m, 4F, F$_{arom}$), 76.74 (m, 4F, F$_{arom}$) ppm. MS m/z: 668 (M$^+$). Analysis Found: C, 50.04%; H; 0.62%; F,22.64%; Cl,21.56% . $C_{28}H_6Cl_4F_8O_2$ 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): ν = 1580, 1495, 1480, 1425 cm^{-1}. Raman (neat): ν = 2220 (C≡C of monomer), 2118, 2085, 2067 (C≡C of polymer) cm^{-1}. ^{1}H NMR (CDCl$_3$/TMS): δ = 6.67 (d, 4 H, H$_{arom}$, J = 8.4 Hz), 7.21 (d, 4 H, H$_{arom}$, J =8.4 Hz) ppm. ^{19}F NMR (CDCl$_3$ /CF$_3$COOH): δ = 57.25 (m, 4F, F$_{arom}$), 76.15 (m, 4F, F$_{arom}$) ppm. MS m/z: 688 (M$^+$). Analysis Found: C, 49.02%; H,1.18%; F,22.43% Br, 23.16%. $C_{28}H_8Br_2F_8O_2$ 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): ν = 1583, 1493, 1469, 1420 cm^{-1}. Raman (neat): ν = 2225 cm^{-1}. ^{1}H NMR (acetone-d$_6$/TMS): δ = 7.00-8.00 (m, H$_{arom}$) ppm. ^{19}F NMR (acetone-d$_6$/CF$_3$COOH): δ = 60.34 (m, 4F , F$_{arom}$), 79.79 (m, 4F, F$_{arom}$) ppm. MS m/z: 620 (M$^+$). Analysis Found: C, 54.10%; H, 1.08%; N, 4.29%; F, 24.99%. $C_{28}H_8F_8N_2O_6$ 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): ν = 1580, 1490, 1482, 1422 cm^{-1}. Raman (neat): ν = 2221 cm^{-1}. ^{1}H NMR (acetone-d$_6$/TMS): δ = 7.34-7.44 (m, Harom) ppm. ^{19}F NMR (acetone-d$_6$/CF$_3$COOH): δ = 60.00 (m, 4F , F$_{arom}$), 78.00 (m, 4F, F$_{arom}$) ppm. MS m/z; 620 (M$^+$). Analysis Found: C, 53.97%; H, 1.05%; N, 4.36%; F, 24.44%. $C_{28}H_8F_8N_2O_6$ 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): ν = 1700, 1600, 1500, 1490, 1430 cm^{-1}. Raman (neat): ν = 2221 cm^{-1}. ^{1}H NMR (DMSO-d$_6$/TMS): δ =

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_3COOH): δ = 59.12 (m, 4 F, F_{arom}), 78.34 (m, 4 F, Farom) ppm. MS m/z: 586 (M^+). Analysis Found: C, 61.38%; H,1.42%; F,26.12%. $C_{30}H_{10}F_8O_4$ Calc.: C, 61.43%; H, 1.71%; F, 25.94%.

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