

Preliminary Note

Novel soluble diacetylene polymers containing fluorophenyl rings

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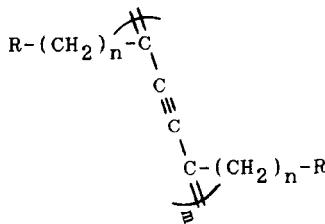
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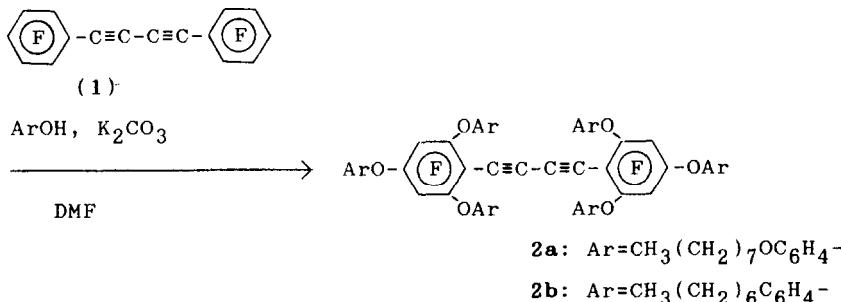
Abstract

Two fluorophenyl-substituted diacetylene compounds, 1,4-bis(2,4,6-triaryloxy-difluorophenyl)butadiynes, have been synthesized, and been shown to have solid-polymerization activity upon exposure to daylight or γ -irradiation. The blue polymers dissolved in normal organic solvents to give transparent solutions with no insoluble remnants. The UV-vis spectra of the solutions indicate broad, structureless absorption from 450 to 620 nm.

Polymers obtained by topochemical [1] polymerization of conjugated diynes are generally insoluble and non-fusible with only few exceptions [2, 3]. The usual methods of polymer analysis, such as viscosity, light scattering and GPC, require dilute solutions and hence these polymers cannot be investigated by such means. One useful method is to attach flexible side-chains to the polymers backbones in order to increase the solubility [4]. Many fluorophenyl-substituted diacetylenes are polymerized readily in the solid state and substituent groups may be readily introduced into the fluorophenyl rings [5, 6]. For this reason, two fluorophenyl-substituted diacetylenes, **2a** and **2b**, have been synthesized with flexible side-chains attached to the fluorophenyl rings. Previous papers have reported the preparation of soluble diacetylene polymers with flexible polymethylene chains between the side-groups and the polymer backbone [7] (see Scheme 1). Polydiacetylenes with aromatic residues directly bound to the main chain and hence with increasing numbers of π -electrons per repeating unit through π -conjugation between the main and side-chains are more rigid and more insoluble. It is noteworthy that the solubility introduced by six flexible chains attached to fluorophenyl rings can overcome the insolubility caused by the rigidity induced by substantial π -conjugation, and lead to soluble polymers.



Scheme 1.



Scheme 2.

TABLE 1
Physical data and elemental analyses of **2a** and **2b**

	M.p. (°C)	IR (KBr) (cm ⁻¹)	¹ H NMR (CDCl ₃ /TMS) (ppm)	¹⁹ F NMR (CDCl ₃ /CF ₃ COOH) (ppm)	MS (m/e)	Elemental analysis [% found (calculated)]
2a	108	2920; 2850; 1505; 1470; 1395; 1295; 1200; 1105; 995; 965; 830	6.64–7.02 (24H, m); 3.88 (12H), t, <i>J</i> =6.1 Hz); 1.10–2.10 (72H, m); 0.89 (18H, t, <i>J</i> =6.1 Hz)	66.97 (s, F arom.)	1596	C, 75.02 (75.26); H, 8.02 (7.95); F, 4.68 (4.76)
2b	83	2923; 2855; 1513; 1478; 1413; 1298; 1227; 1114; 985; 972; 844	7.02–7.42 (24H, m); 2.30 (12H, t, <i>J</i> =5.8 Hz); 1.15–2.20 (60H, m); 0.85 (18H, t, <i>J</i> =5.8 Hz)	67.12 (s, F arom.)	1414	C, 80.12 (79.77); H, 8.23 (8.06); F, 5.30 (5.37)

The syntheses of monomers **2a** and **2b** are shown in Scheme 2 and their physical data are listed in Table 1. The UV-vis spectra of polymer solutions of **2a** and **2b** are depicted in Figs 1 and 2.

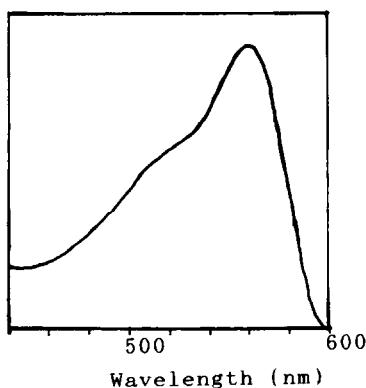


Fig. 1. UV-vis spectrum of polymer **2a** dissolved in CCl_4 .

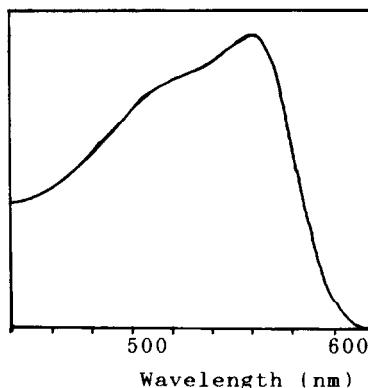


Fig. 2. UV-vis spectrum of polymer **2b** dissolved in CHCl_3 .

Crystals of the monomers **2a** and **2b** turn blue on exposure to daylight or γ -irradiation. The blue polymers dissolve in normal organic solvents, such as CHCl_3 , CCl_4 , cyclohexane, etc., to yield red transparent solutions. When non-solvents, such as CH_3OH and $\text{C}_2\text{H}_5\text{OH}$, are added to the red solutions the latter turn blue once more. On increasing the amount of non-solvent in such solutions particularly when concentration of the latter is high, a blue solid may be precipitated.

In previous papers [5, 6], we have reported the synthesis of 1,4-(bis-pentafluorophenyl)butadiynes (**1**). Here we report the synthesis of monomers **2a** and **2b**. The polymerization and other properties of the soluble polymers are now being studied further.

1,4-Bis[2,4,6-tri(4-octophenoxy) difluorophenyl]butadiynes (**2a**) were typically synthesized by adding 4-octyloxyphenol (209 mg, 0.942 mmol) to a stirred solution of 1,4-bis(pentafluoro)butadiyne (**1**) (60 mg, 0.157 mmol) and K_2CO_3 (1.2 g, 8.7 mmol) in DMF (5 ml). After 48 h at 30–35 °C, the mixture was diluted with aq. NaOH (10 ml, 1.5 M) to yield a yellowish precipitate. Recrystallization from acetone–methanol gave white crystals of 1,4-bis[2,4,6-tri(octophenoxy) difluorophenyl]butadiynes (**2a**) (230 mg, yield 92%).

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