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PRELIMINARY NOTE

Synthesis of Poly(1,4-Tetrafluorophenylene-ethynylene) by Nucleophilic Substitutions on 1-Pentafluorophenyl-2-trimethylsilylacetylene

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SUMMARY

New polymers with a linear conjugated backbone built up by the alternating combination of tetrafluorophenylene with ethynylene units, poly(1,4-tetrafluorophenylene-ethynylene) have been prepared by nucleophilic substitution on 1-pentafluoro-phenyl-2-trimethylsilylacetylene using 4-Cl-C_6H_4-OK and 4-Br-C_6H_4-OK as bases and nucleophilic initiators.

Rigid rod-like polymers with a linear conjugated backbone, such as polydiacetylenes [1,2], polyacetylenes [3,4], poly(1,4-phenylene)s [5], and poly(1,4-phenylene-ethylene)s [6-8], have attracted much attention for their unique properties, such as conductivity, optical nonlinearity, heat stability and photoconductivity. In our present study, poly(1,4-tetrafluorophenylene-ethynylene) was obtained easily from 1-pentafluorophenyl-2-trimethylsilylacetylene by nucleophilic substitution. Poly(1,4-phenylene-ethylene)s have generally been prepared either by the Pd-catalyzed self-coupling of a bromophenylacetylene, or by the Pd-catalyzed coupling of a 1,4-diethynylbenzene with 1,4-dibromobenzene [6,9]. In this note, we wish to describe the first synthesis of poly(1,4-tetrafluorophenylene-ethynylene) by nucleophilic substitutions on 1-pentafluorophenyl-2-trimethylsilylacetylene using 4-Cl-C_6H_4-OK and 4-Br-C_6H_4-OK as bases and initiators.

Previously, we have reported that nucleophilic substitutions on 1-pentafluorophenyl-2-trimethylsilylacetylene (1) with various nucleo-

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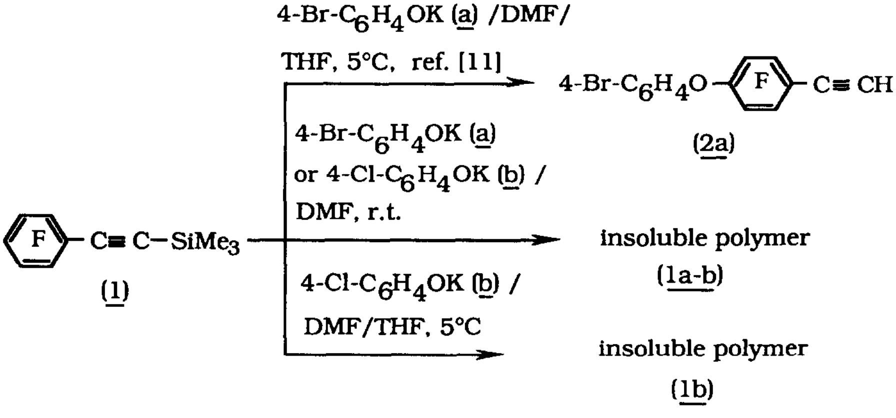
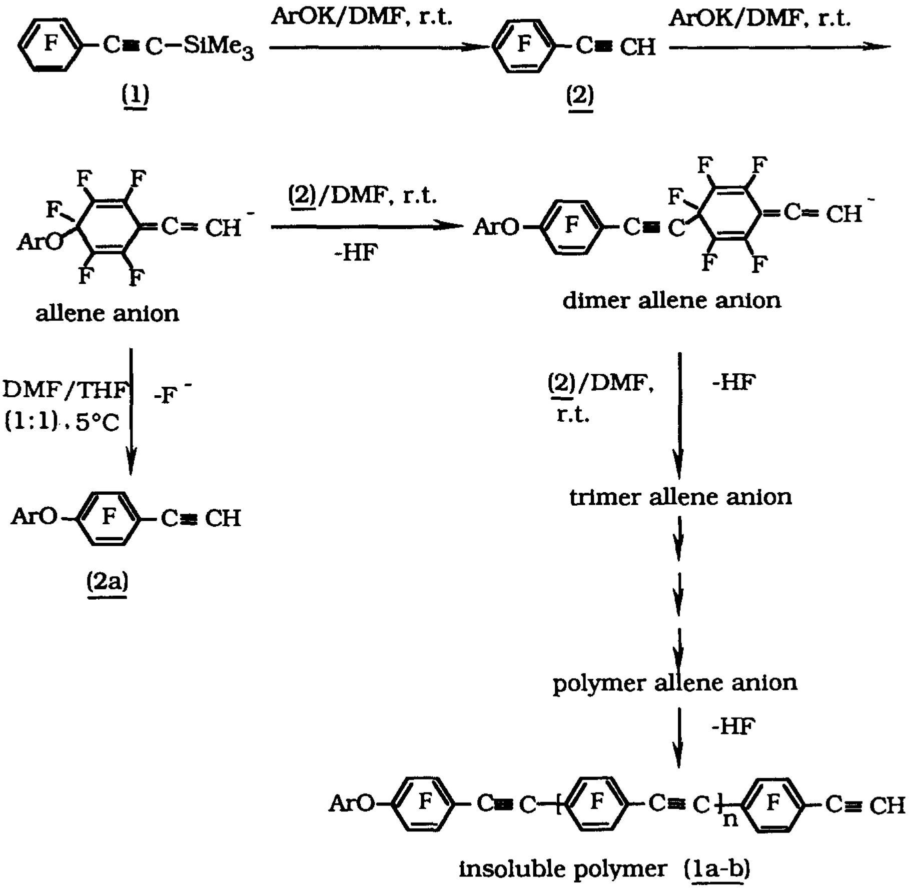
philes gave p-substituted products in good yields [10,11]. But when 4-Br-C_6H_4OK (a) and 4-Cl-C_6H_4OK (b) were used as nucleophiles, the reactions of them with (1) in DMF at room temperature gave only brown insoluble polymers. We found that (a) reacted with (1) in DMF/THF (1:1) at 5°C to give the p-substituted product, p-(4-bromophenoxy)tetrafluorophenylacetylene in good yield [11]. However, (b) reacted with (1) in DMF/THF (1:1) at 5°C to give only insoluble polymer (Scheme 1).

Commonly, poly(1,4-phenylene-ethynylene)s are completely insoluble, which is the reason for the lack of proper analytical and spectroscopic characterisation of these macromolecular substances. Here, the insoluble polymers were characterized as poly(1,4-tetrafluorophenylene-ethynylene)s by IR and analysis. Fig. 1 showed a typical infrared spectra for insoluble polymer (1a). The absorption at 2210 cm^{-1} is a typical C≡C stretching frequency in acetylenic compounds. In the spectra of this insoluble polymer (1a), a band also appears at 3301 cm^{-1} which corresponds to the absorption frequency of the C≡C-H stretching in a terminal acetylene. The absorption at 1479 cm^{-1} in the infrared spectra is ascribable to 1,4-substituted-tetrafluorobenzene.



Scheme 1.

A plausible mechanism for the polymerization of 1-pentafluorophenyl-2-trimethylsilylacetylene (1) using 4-Br-C_6H_4-OK (a) and 4-Cl-C_6H_4-OK (b) as bases and initiators is outlined in Scheme 2. In the first step, the trimethyl silyl group was removed from (1) to give pentafluorophenylacetylene (2), and this was followed by the formation of a Wheland-type intermediate, an allene anion which gave p-(4-bromo-phenoxy)tetrafluorophenylacetylene (2a) after removal of F⁻. This allene anion could also react as a nucleophile with pentafluorophenylacetylene (2) and at the same time HF was removed, to give a new dimer allene anion which could react in turn with pentafluorophenylacetylene (2) to give a trimer allene anion. In this way, we could obtain poly(1,4-tetrafluorophenylene-ethynylene) (1a-b), eventually.



Ar= 4-Cl-C_6H_4-, 4-Br-C_6H_4-

Scheme 2 .

TABLE 1

Preparation of poly(1,4-tetrafluorophenylene-ethynylene) (1a-b) from 1-pentafluorophenyl-2-trimethylsilylacetylene (1)

Nucleophilic initiator a-b	Reaction condition solvent/temp./time	Insoluble polymer (1a-b) No	Yield (%)
a 4-Br-C_6H_4OK	DMF/r.t./60min[a]	1a	71
b 4-Cl-C_6H_4OK	DMF/r.t./45min	1b	75
b 4-Cl-C_6H_4OK	DMF/THF(1;1)/ 5°C/90min	1b	73

[a] 4-Br-C_6H_4OK reacted with (1) in DMF/THF (1:1) at 5°C to give p-(4-bromo-phenoxy)tetrafluorophenylacetylene in good yield [11].

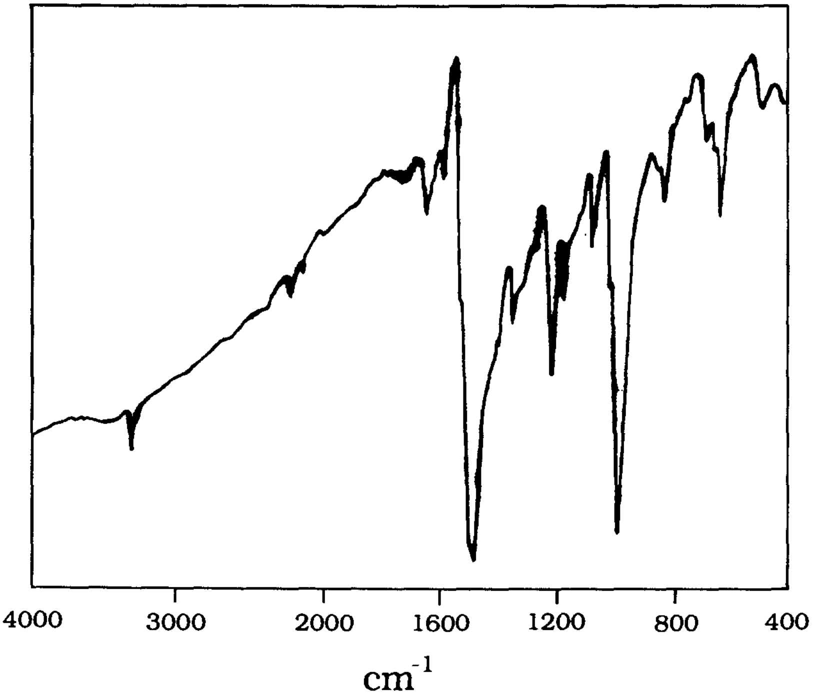


Fig. 1. Infrared spectra of insoluble polymer (1a).

Poly(1,4-tetrafluorophenylene-ethynylene) (1a): A Typical Procedure: To a solution of 1-pentafluorophenyl-2-trimethylsilylacetylene (1; 1g, 3.8mmol) in DMF (10ml) at room temperature was added 4-Br-C_6H_4OK (a; 0.8g, 3.8mmol) dropwise. A blue solution was formed initially, followed by the evolution of a lot of heat and precipitation of insoluble polymer. After 60 min, the mixture was diluted with water (20ml). The brown insoluble polymer was collected and washed with acetone. This polymer, poly(1,4-tetrafluorophenylene-ethynylene) (1a), was dried in vacuo at room temperature; Yield: 71%. IR (KBr): 3301, 2210, 1636, 1479, 1338, 1203, 1164, 1068, 984, 821, 625 cm^{-1}; Analysis, Found: C 51.92%, H 0.45%, F 40.82%, Br 6.53; Calc. for $C_{54}H_5BrF_{24}O$: C 53.78%, H 0.41%, F 37.84%, Br 6.53%.

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