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Synthesis of Deeply Colored Soluble Polyacetylenes from 1-Ethynylnaphthalene and 3,6-Dibutyl-9-ethynylphenanthrene

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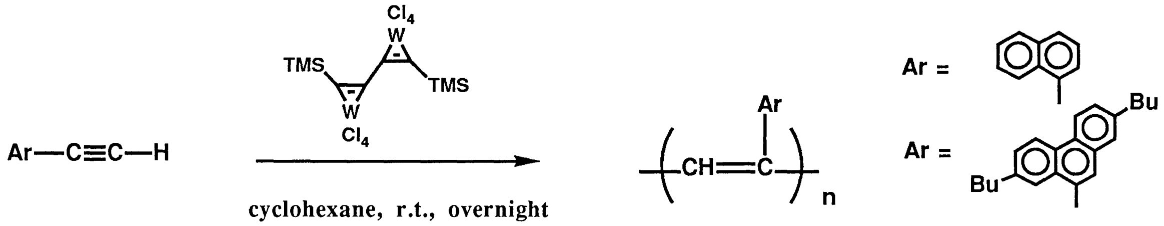
Deeply colored soluble polyacetylenes were synthesized from 1-ethynylnaphthalene and 3,6-dibutyl-9-ethynylphenanthrene by employing a tungsten (IV) catalyst. Since 2-ethynylnaphthalene gave the less conjugated polymer, connection mode of the aromatic pendants was found to be essential for maintaining the conjugated structure of the polyene chain. Electrochromic properties of poly(1-ethynylnaphthalene) were also studied.

Recently, we reported the synthesis and the polymerization of substituted *o*-trimethylsilylphenylacetylenes with a tungsten (IV) catalyst,[1] and the presence of an appropriate size of *ortho*-substituent was proved to be essential for the formation of highly conjugated polyene structure. Since 1-ethynylnaphthalene (**1**) can be regarded as an *ortho*-substituted phenylacetylene, the polymerization of **1** and the related compounds has been studied here (Scheme 1).



Scheme 1.

When **1** was treated with 5 mol% of a tungsten complex[1] in cyclohexane overnight, poly(1-ethynylnaphthalene) (**2**) was obtained in 90% yield as black powder. Anal. Calcd for $C_{12}H_8$: C; 94.70, H; 5.30%. Found: C; 93.45, H; 5.58%. The polymer is soluble in THF, $CHCl_3$, CH_2Cl_2, and benzene, while insoluble in MeOH, hexane, and CH_3CN. Reddish purple $CHCl_3$ solution of **2** has an absorption maximum at 509 nm showing a considerable level of conjugation in polyene chain. As shown in Table 1, 2-ethynylnaphthalene which lacks the *ortho*-substituent gave a polymer with substantially shorter effective conjugation.[2] 9-Ethynylphenanthrene and 1-ethynylpyrene containing the same partial structure with **1** also gave deeply colored polymers, mostly insoluble in organic solvents. Then, alkyl groups were introduced to the pendant in order to improve the solubility. 3,6-Dibutyl-9-ethynylphenanthrene (**3**) was prepared from 3,6-dibromophenanthrene as follows:[3] i) BuMgBr, Ni(dppp)Cl_2, ether, refl., 20 h, 56%;[4] ii) Br_2, CCl_4, 0 °C, 10 min, 52%; iii) KI, CuI, HMPA, 150 °C, 6 h, 95%;[5] iv) HC≡CTMS, $Pd_2(dba)_3$, PPh_3, CuI, Et_3N, C_6H_6, 80 °C, 3 h; v) TBAF, THF, r.t., 2 h, 82% in 2 steps. Polymerization of **3** gave a soluble polymer with the absorption maxima at 548 nm (Table 1). Whereas reported polymerization of ethynylated polycyclic aromatic hydrocarbons were rather inefficient,[6] we can now synthesize the deeply colored soluble polyacetylenes with condensed polycyclic aromatic pendants quite efficiently by using a tungsten catalyst.

Table 1. Synthesis of Polyacetylenes with Condensed Polycyclic Aromatic Pendants.

Acetylene	Yield/%	MW_n (x 10^{-3})a)	Color of powder	UV-VIS λ_{max}/nm (log ε) in $CHCl_3$
1-Ethynylnaphthalene (**1**)	90	95	black	509 (3.7), 287 (3.8)
2-Ethynylnaphthalene	80	35	dark red	b)
3,6-Dibutyl-9-ethynylphenanthrene (**3**)	quant.	20	black	548 (3.5)

a) Determined by GPC method with polystyrene standard employing THF as the solvent. b) No absorption maxima observed above 300 nm.

A spin-coated film of **2** on an ITO glass exhibited electrochromic interconversion between the reddish purple state and oxidized colorless state (Fig. 1). Cyclic voltammetry showed two oxidation waves at +0.24 and +1.24 V vs. Ag/AgCl (Fig. 2). Compared with the reported electrochromic behavior of poly(*o*-trimethylsilylphenylacetylene),[7] **2** is characterized by the more negative first oxidation potential and the presence of the second oxidation wave.

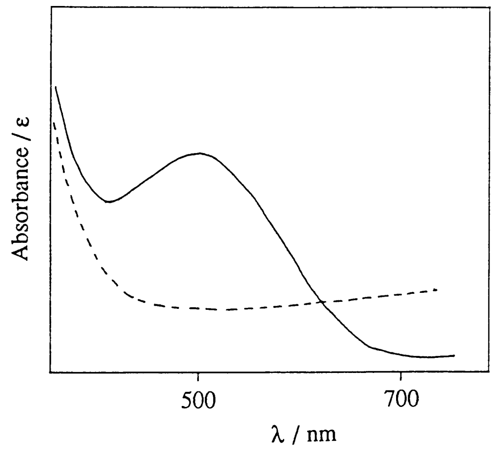


Fig. 1. UV-VIS spectra of a spin-coated film of **2** on an ITO glass in the neutral (—) and oxidized state (---).

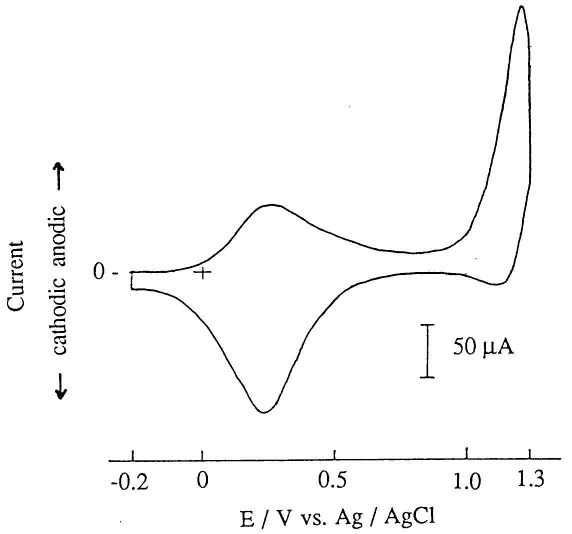


Fig. 2. Cyclic voltammogram of a film of **2** on an ITO glass in 0.1M $LiClO_4$-CH_3CN at the scan rate of 0.1 V/s.

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