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Desilylation Reactions of Poly[(*t*-butyldimethylsilyloxy)phenylacetylene]s

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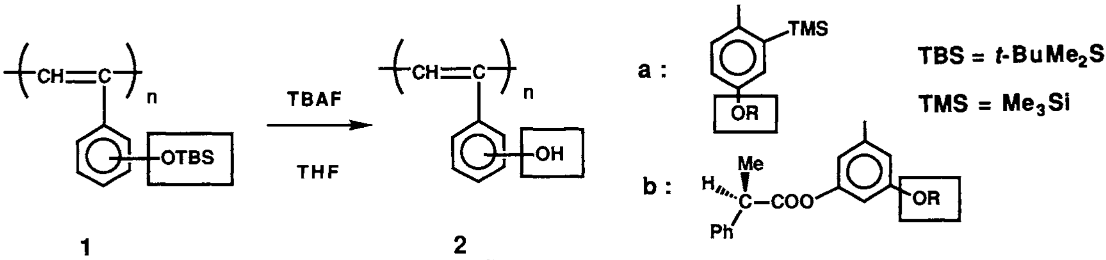
Poly[4-(*t*-butyldimethylsilyloxy)-2-trimethylsilylphenylacetylene] and poly[5-ethynyl-3-(*t*-butyldimethylsilyloxy)phenyl (R)-2-phenylpropionate] were desilylated with Bu_4NF in THF. The solution changed its color depending on the structure of the aromatic pendants.

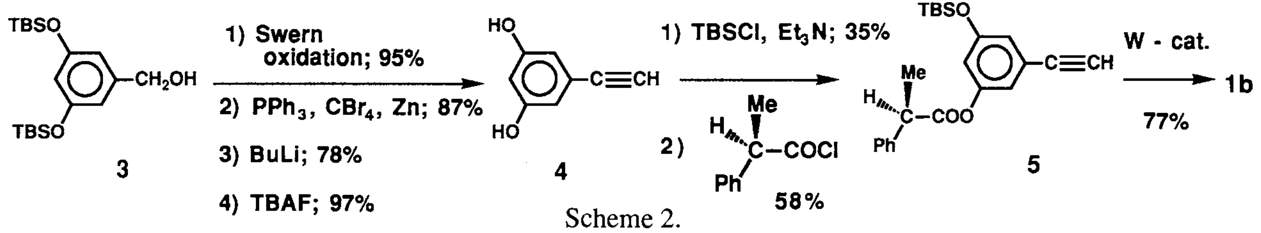
Previous studies on the synthesis and the properties of substituted poly(arylacetylene)s have revealed that an appropriate size of *ortho*-substituent on the aromatic ring was essential to maintain a highly conjugated polyene structure.1) Accordingly, it was anticipated that chemical transformations on the pendants which could vary the size of substituents would perturb the conjugated state of the polyene main chain resulting in the color change. In order to test the idea, desilylation reactions of poly[(*t*-butyldimethylsilyloxy)phenylacetylene]s were investigated (Scheme 1).



Scheme 1.

When poly[4-(*t*-butyldimethylsilyloxy)-2-trimethylsilylphenylacetylene] (**1a**)1) in THF was treated with excess Bu_4NF (TBAF), the solution turned its color from *red to reddish purple*. The desilylated polymer **2a** was obtained by washing the solution with saturated aq NH_4Cl and water, drying, and removing the solvents in vacuo. UV (THF) λ_{max} (log ε) **1a**: 494 nm (3.6), **2a**: 519 nm (3.3). A strong O-H band (3475 cm^{-1}) was observed by IR spectra of **2a**, and its solubility to organic solvents showed hydrophilic character: Soluble in THF, methanol, and ethanol. Insoluble in $CHCl_3$, C_6H_6, and CH_3CN. MW_n of **2a**, 1.3×10^5, as determined by GPC method showed that serious main chain scission did not take place during the desilylation of **1a**, MW_n 3.7×10^5.

Next, poly[5-ethynyl-3-(*t*-butyldimethylsilyloxy)phenyl (R)-2-phenylpropionate] (**1b**) was prepared from a known benzyl alcohol **3**3) (Scheme 2), and was desilylated. The chiral *m*-substituent was expected to function as a probe of the conformation change at the main chain. Dihydroxyethynylbenzene **4**, synthesized from **3** by a 4-steps transformation, was converted to a monosilyl ether by treating with 1 equivalent of TBSCl and Et_3N (CH_2Cl_2, 8.3 h, r. t.) followed by separation of unreacted **4** and bis-silylated compound. Then, the other phenolic hydroxy group was esterificated (pyridine-CH_2Cl_2, 0 °C, 40 min) with an acid chloride prepared from commercially available (R)-2-phenylpropionic acid (88%ee determined by HPLC as the methyl ester) and oxalyl chloride in CH_2Cl_2 at 0 °C. HPLC analysis of the ester **5** indicated essentially no racemization during the esterification. $[\alpha]_D^{24}$ -59.8°(c 1.01, $CHCl_3$). Polymerization was carried out as before[1] giving **1b** in 77% yield. IR (KBr) 1760 (C=O), 835 (Si-Me) cm^{-1}. UV (THF) λ_{max} (log ε) 495 nm (3.6). MW_n 1.1×10^5 (GPC). CD (THF) λ_{ext} 490 nm ([θ] 1500), 400 (0), 347 (-1100), 314 (0), 278 (2600), 246 (0). The magnitude of the CD effect is the same order with known chiral polyacetylenes, the main chain of which were considered to be twisted predominantly in one-sense by the chiral side groups.[4, 5] We therefore assume a similar helical structure for **1b**. On desilylation, a THF solution of **1b** changed its color from *red to orange* (Fig. 1) giving **2b**. UV λ_{max} (log ε) 433 nm (3.3) in THF, and 442 nm (3.3) in MeOH. Solubility behavior of **2b** was similar to that of **2a**. Presence of O-H and C=O group (3418, 1756 cm^{-1}) and considerable reduction of intensity at 835 cm^{-1} by IR indicated selective removal of the silyl group without effecting the ester moiety. As shown by disappearance of the CD effect above 300 nm (Fig. 2), a drastic conformation change was induced by the desilylation.



Scheme 2.

The different color change of **1a** and **1b** on the desilylation may be explained as follows. Since the highly conjugated main chain of **1a** is sustained by the *ortho*-TMS group, the removal of the *para*-TBS group induces a relatively small conformation change. In contrast, the desilylation of the *meta*-TBS group of **1b**,which is essential for the conjugated state, turns the main chain to a considerably less conjugated structure. Although these color change processes are irreversible, the knowledge obtained here will be useful to design materials, which respond to chemical or physical stimulation.

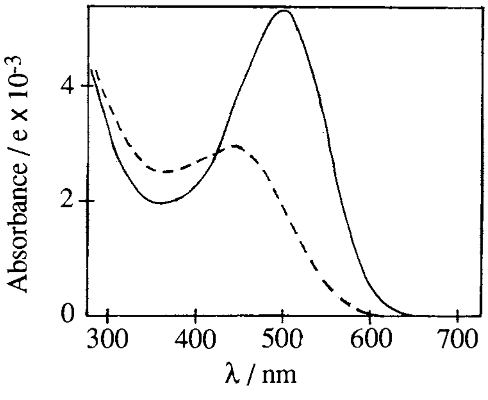


Fig. 1. UV-VIS spectra of **1b** (—) and **2b** (---) in THF at 2.5×10^{-5} M.

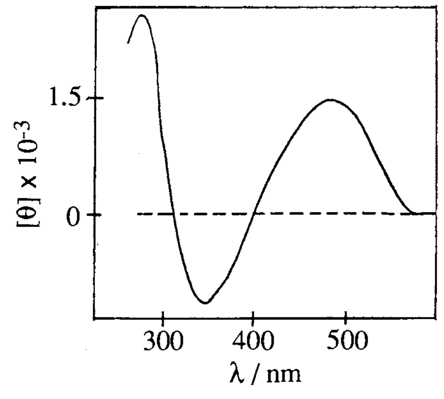


Fig. 2. CD spectra of **1b** (—) and **2b** (---) in THF at 1.8×10^{-3} M.

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