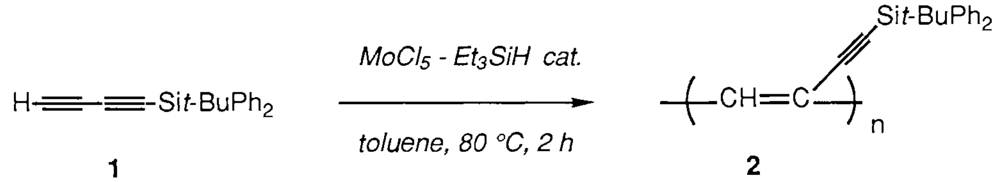
CHEMISTRY LETTERS, pp. 2221-2222, 1990.

Synthesis of a Widely Conjugated, Substituted Polyacetylene from 1-*t*-Butyldiphenylsilyl-1,3-butadiyne

Masahiko YAMAGUCHI,* Kazuhiko TORISU, Ken-ichi HIRAKI, and Toru MINAMI
Department of Applied Chemistry, Kyushu Institute of Technology,
Sensui-cho, Tobata, Kitakyushu 804

Polymerization of 1-*t*-butyldiphenylsilyl-1,3-butadiyne with $MoCl_5$-Et_3SiH catalyst gives a novel widely conjugated polyacetylene. An appropriate selection of the silyl group and catalyst is essential.

The solid phase photopolymerization of 1,3-butadiynes are known to proceed in 1,4-manner, and the physical properties of the conjugated polyenyne compounds have been extensively studied.1) Recently, trials to obtain 1,2-addition-type polymers from mono-silylated butadiyne were reported resulting in the low molecular weight less-conjugated products.2) We, however, found that a widely-conjugated polymer with higher molecular weight and a regular structure can be synthesized by an appropriate selection of the silicon substituent and catalyst.



1 **2**

Scheme 1.

A typical polymerization procedure of 1-*t*-butyldiphenylsilyl-1,3-butadiyne (**1**)3) is as follows: Under a nitrogen atmosphere, a toluene (0.2 ml) suspension of $MoCl_5$ (23 mg, 0.09 mmol) and Et_3SiH (7 mg, 0.05 mmol) was stirred at 30 °C for 15 min. Then, a toluene (1 ml) solution of **1** (187 mg, 0.65 mmol) was added, and stirring was continued at 80 °C for 2 h. Chloroform was added to the mixture, and a small amount of insoluble inorganic materials were removed by filtration. After the solvents were evaporated, poly-(1-*t*-butyldiphenylsilyl-1,3-butadiyne) (**2**) (96 mg, 59 %) was precipitated by adding hexane (or methanol).

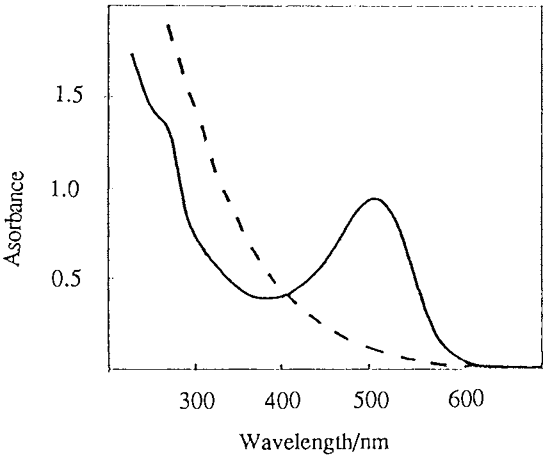


Fig. 1. The UV-VIS Spectra of **2** (—)(1.1 mg/20 mL) and poly-(*t*-Butyldimethylsilyl-1,3-butadiyne) (- - -)(0.9 mg/20 mL) in $CHCl_3$

The polymer was soluble in chloroform, toluene, or THF, and insoluble in hexane and methanol. The UV-VIS spectra of **2** (λ_{max} 510 nm) indicated the widely conjugated structure of this polymer (Fig. 1). Although the group 5 and 6 transition metal compounds are known to catalyze the polymerization of substituted acetylenes, the resulted polymers generally possessed the less conjugated structure.4) Accordingly, the polymer **2** provides an exceptional example to this group of substances.5) The comparison of ^{1}H-NMR of the monomer and the polymer showed high field shift of *t*-butyl and phenyl protons: **1**; ^{1}H-NMR ($CDCl_3$) δ 1.10 (9H,s), 2.17 (1H,s), 7.2-7.5 (6H,m), 7.5-7.8 (4H,m). **2**; ^{1}H-NMR ($CDCl_3$) δ 0.84 (9H,brs), 6.7-7.3 (6H,m), 7.3-7.8 (4H,m). Two olefinic carbons at δ 120.6, 140.0 and acetylenic carbons at δ 96.3, 106.5 observed in the ^{13}C-NMR spectra in $CDCl_3$ exhibited that the polymerization proceeded regularly at the terminal triple bond.$^{6)}$ The IR spectra showed the presence of acetylenic unit (2140 cm^{-1}), and the elemental analysis agreed well with the calculated values: Anal. Calcd for $C_{20}H_{20}Si$: C; 83.27, H; 6.99 %. Found: C; 82.96, H; 6.99 %. The MW_n was estimated to be 31×10^3 by GPC method, which is considerably higher than the previously reported polymers of the silylated butadiynes.$^{2)}$

The use of other metathesis catalysts, WCl_6, $TaCl_5$, $NbCl_5$ *etc.*, or Ziegler-Natta catalysts, $Ti(OR)_4$-Et_3Al, $TiCl_4$-Et_3Al, did not give the high molecular weight polymer from **1**. It was also found that the selection of the *t*-butyldiphenylsilyl protecting group was important, and widely conjugated polymers were not obtained from Et_3Si, *t*-BuMeSi-, or Ph_3Si-derivatives (Table 1). The ^{13}C-NMR spectra of these polymers showed broad peaks of acetylenic or olefinic carbons suggesting the irregularity in the structure.

Table 1. The Effects of the Silicon Substituents on the Polymerization of Silylated Butadiynes

R_3Si	Yield/%	MW ($\times 10^3$)$^{a)}$	Color	UV λmax/nm in $CHCl_3$
$Et_3Si^{b)}$	66	< 3.1	brown	c)
t-$BuMe_2Si$	70	< 3.1	brown	c)
Ph_3Si	54	< 3.1	brown	c)
t-$BuPh_2Si$	59	31	red	510

a) Determined by GPC method with THF as the solvent. b) Also see Ref. 2a, b). c) No distinct absorption maxima observed (see Fig. 1).

Financial support from the Japan Securities Scholarship Foundation is gratefully acknowledged. We would also like to thank the Shin-Etsu Chemical Co., Ltd for the generous gift of silicon reagents.

References

1) H. Bässler, *Adv. Polym. Sci.*, **63**, 1, (1984); V. Enkelmann, *ibid.*, **63**, 91 (1984). 2) a) N. Kobayashi, M. Nakada, E. Tsuchida, H. Matsuda, H. Nakanishi, and M. Kato, *J. Polym. Sci., Polym. Lett.*, **24**, 215 (1986); b) N. Kobayashi, M. Nakada, H. Ohno, E. Tsuchida, H. Matsuda, H. Nakanishi, and M. Kato, *New Polymeric Mat.*, **1**, 3 (1987); c) M. Ozaki, Y. Ikeda, and I. Nagoya, *Synth. Metals*, **18**, 485 (1987). 3) For the preparation of **1**: M. Yamaguchi, K. Torisu, S. Nakamura, and T. Minami, submitted. 4) A review; T. Masuda and T. Higashimura, *Adv. Polm. Sci.*, **81**, 121 (1987). 5) It was recently reported that *o*-substituted phenylacetylenes gave a widely conjugated polymer with an absorption maxima at about 460 nm: T. Masuda, M. Kawasaki, T. Hamao, T. Higashimura, T. Ueda, and H. Muramatsu, *Macromolecules*, **21**, 281 (1988); Y. Abe, T. Masuda, and T. Higashimura, *J. Polym. Sci., Part A, Polym. Chem.*, **27**, 4267 (1989). 6) The comparison of the chemical shift of the acetylenic carbons of *cis*-1-phenylthio-4-*t*-butyldiphenylsilyl-1-buten-3-yne, synthesized by the addition of thiophenol to **1**, also supported the 1,2-adduct structure: ^{13}C-NMR ($CDCl_3$) δ 98.7, 104.9.

(Received September 13, 1990)