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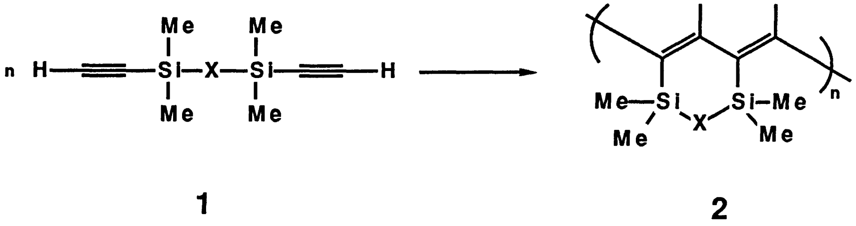
Polymerization of Monomers Containing Two Ethynyldimethylsilyl Groups

Tetsuo KUSUMOTO and Tamejiro HIYAMA*
Sagami Chemical Research Center, 4-4-1 Nishiohnuma, Sagamihara, Kanagawa 229

Polymerization of $(HC{\equiv}CSiMe_2)_2X$ with WCl_6 or $MoCl_5$ catalyst afforded polymers soluble in common organic solvents. The conductivity of the polymer fell in the range of insulators but was improved to 10^{-2} S·cm^{-1} upon doping with $(Et_2N)_3S^+ SiF_2Me_3^-$ (or *n*-$Bu_4N^+ F^-$) and I_2 (or SO_3).

Conjugated polyenes such as polyacetylene and polydiacetylene have salient physical properties[1,2] like conductivity or semiconductivity, paramagnetism, energy transfer, thermochromism, gas permeability as well as chemical reactivity to form complex with metal. In spite of the promising properties, the instability of these polymers to atmospheric oxygen limited their use. Polymers of substituted acetylenes, *e.g.* poly(trimethylsilylacetylene) and poly(phenylacetylene), endow the remarkable stability at the total expense of the conductivity. Of various structural variations of the alternating conjugated double bond system, poly(1,6-heptadiyne), which has been prepared by cyclopolymerization of the monomer, is noticeable in view of improved stability and workability in addition to fair level of conductivity.[3] We report herein synthesis of soluble, air-stable and conductive polymers by cyclopolymerization of its silicon analogs and homologs of the structure $(HC{\equiv}CSiMe_2)_2X$ (**1**).

The monomers **1a-d** were prepared by the reaction of ethynylmagnesium bromide with $(ClSiMe_2)_2X$ and purified by fractional distillation through a spinning-band still apparatus.[4] A typical procedure for polymerization follows. In a glass flask were placed freshly distilled 1,2-diethynyl-1,1,2,2-tetramethyl-disilane (**1a**, X = bond) (1.00 g, 6.0 mmol), tungsten(VI) chloride (70 mg, 0.68 mmol), and toluene (10 ml).[5] The mixture was heated at 80 °C for 24 h and then poured into methanol (200 ml). Brownish yellow powder (0.42 g) precipitated which was filtered and dried under reduced pressure. The polymer (**2a**) was soluble in toluene, tetrahydrofuran (THF), and chloroform but insoluble in such protic solvents as methanol, ethanol, and water. The ready solubility in the common aprotic organic solvents suggests that the degree



of crosslinking is low and that the cyclopolymerization took place as expected. Its molecular weight estimated by GPC (polystyrene calibration) and viscosity were $\overline{Mn}$ = 6700, $\overline{Mw}$ = 13000 (run 1 of Table 1), and [η] = 0.22, respectively. In addition to WCl_6, $MoCl_5$ and the catalyst system which consists of these metal salts and tetraphenyltin induced the polymerization, but $NbCl_5$ or $TaCl_5$ gave only a small amount of methanol-insoluble polymers. Results are summarized in Table 1. The polymer of **1a** prepared with $MoCl_5$ catalyst was partially insoluble in toluene and THF (run 2). A Ziegler-type catalyst Ti(O*n*-Bu)$_4$-$AlEt_3$ was totally inactive.

In a similar manner the monomers **1b-e** were polymerized with tungsten(VI) chloride catalyst (1.6-3.5 mol%) to give polymers **2b-e**6) fairly stable to air and light except **2d** whose molecular weight was the highest among these but, upon exposure to air for 2 weeks, fell down to $\overline{Mn}$ = 2800 and $\overline{Mw}$ = 3900. Though all the polymers form inflexible film, the flexibility was apparently improved by treatment with tetrabutylammonium fluoride (TBAF) or tris(diethylamino)sulfonium difluorotrimethylsilicate (TASF).

Conductivities (σ) of the polymers **2a-e** were measured in a form of film or pellet and listed in Table 2. The polymers themselves proved to be insulators but grew semiconductors by doping with iodine or sulfur trioxide. The increase of the σ was roughly 10^3-10^6 times. In addition, treatment of the polymers with TBAF or TASF much improved the conductivity in the order of 10^2 to 10^3. Further doping with iodine finally gave semiconductive polymers of 10^{-2} to 10^{-3} $S \cdot cm^{-1}$.7) Although the precise mechanism of the doping with F^- reagents like TBAF and TASF remains yet to be

Table 1. Polymerization a) of **1a-e**

Run	Monomer	Catalyst (mol%)	Polymer	Yield/%	$\overline{Mn}$ b)	$\overline{Mw}$ b)
1	X = bond (**1a**)	WCl_6 (2.9)	**2a** brownish yellow c,d)	42	6700	13000
2	X = bond (**1a**)	$MoCl_5$ (1.9)	**2a** brown e)	30	15000	26000
3	X = bond (**1a**)	$NbCl_5$ (1.1)	**2a** pale brown d)	11	5700	8800
4	X = bond (**1a**)	WCl_6 (4.3) - $SnPh_4$ (2.6)	**2a** brownish yellow d)	52	4200	7600
5	X = bond (**1a**)	$MoCl_5$ (2.6) - $SnPh_4$ (1.5)	**2a** brown d)	27	4900	8600
6	X = bond (**1a**)	Ti(O*n*-Bu)$_4$ (1.3) - Et_3Al (5.1)		0		
7	X = CH_2 (**1b**)	WCl_6 (3.5)	**2b** brownish red d)	32	6500	16000
8	X = CH_2CH_2 (**1c**)	WCl_6 (1.6)	**2c** brownish yellow d)	22	11800	36600
9	X = $SiMe_2$ (**1d**)	WCl_6 (2.2)	**2d** brownish yellow d)	42	12000	1560
10	X = O (**1e**)	WCl_6 (1.9)	**2e** brownish yellow d)	63	9200	14800

a) Polymerization was carried out at 80 °C in toluene as the solvent undder a nitrogen atmosphere. b) Estimated by GPC (polystyrene calibration). c) Spectral data are given in Ref. 6. d) Soluble in toluene and THF. e) Partly soluble in toluene and THF.

Table 2. Conductivities of Polymers **2a-e**

Polymer	Form	σ (S·cm^{-1})[d]	Dopant[e]	σ (S·cm^{-1})[d,f]
2a	inflexible film[a]	5.5×10^{-9}	I_2	2.8×10^{-3}
2a			SO_3	9.4×10^{-4}
2a/TASF[c]	flexible film[a]	3.5×10^{-6}	I_2	2.3×10^{-3}
2b	pellet[b]	8.6×10^{-9}	I_2	7.1×10^{-3}
2b/TASF[c]	film[a]	1.3×10^{-5}	I_2	2.7×10^{-2}
2c	inflexible film[a]	6.7×10^{-9}	I_2	1.2×10^{-3}
2c/TBAF[c]	film[a]	7.2×10^{-7}	I_2	1.7×10^{-3}
2d	inflexible film[a]	3.7×10^{-9}	I_2	1.9×10^{-3}
2d/TASF[c]	film[a]	2.0×10^{-8}	I_2	2.6×10^{-2}
2e	inflexible film[a]	4.8×10^{-8}	I_2	8.6×10^{-5}
2e/TASF	inflexible film[a]	5.8×10^{-6}	I_2	2.0×10^{-3}

a) Prepared by casting the toluene solution of the polymer. b) Prepared by pressing the powdered polymer with the aid of KBr disc die under 200 atm. c) A THF solution of TASF or TBAF (10 wt%) was treated with the polymer dissolved in THF. d) Measured by the 2-point-probe method. e) The polymer film or pellet was exposed with the vapor of the dopant. The amount of iodine was 1.3 to 2.7 I per one monomer unit. f) Maximum value is shown.

studied, the new method of doping is found to improve both flexibility and conductivity of the film derived from the silyl substituted polyacetylenes.

It is worthy of note that the conformation of the conjugated polymer is locked as such to some extent by the loop $-SiMe_2-X-SiMe_2-$ and thus the conductivities of these polymers are apparently better than those of poly(trimethylsilylacetylene) or poly(1-trimethylsilylpropyne).[5] As the silicon substituted polymers have in general a wide variety of physical and chemical properties, a wide variety of applications are expected. Studies on these lines are in progress in our Laboratories.

References

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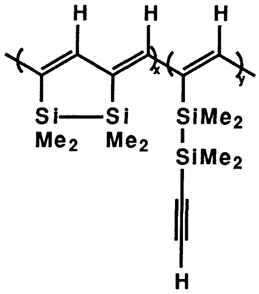
3) H. W. Gibson, F. C. Bailey, A. J. Epstein, H. Rommelmann, S. Kaplan, J. Harbour, X. -Q. Yang, D. B. Tanner, and J. M. Pochan, J. Am. Chem. Soc., 105, 4417 (1983); J. M. Pochan, H. W. Gibson, and J. Harbour, Polymer, 23, 435 (1982); H. W. Gibson and R. J. Weagley, British Polym. J., 18, 120 (1986); R. Zemach, Z. Vardeny, O. Brafman, E. Ehrenfreund, A. J. Epstein, R. J. Weagley, and H. W. Gibson, Mol. Cryst. Liq. Cryst., 118, 423 (1985).

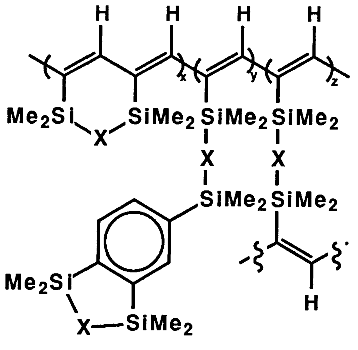
4) Monomers **1a** (L. Birkofer and R. Stilke, Chem. Ber., 107, 3717 (1974) and **1b** (N. P. Kuznetsova and S. D. Lyukas, Zh. Obsch. Khim., 38, 171 (1968); Chem. Abstr., 69, 96811p) respectively were prepared according to the literature. New monomers **1c** and **1d** were prepared by the reaction of ethynylmagnesium bromide (2.3 mol) with the corresponding dichlorides $ClSiMe_2CH_2CH_2SiMe_2Cl$ and $ClSiMe_2SiMe_2SiMe_2Cl$, respectively, at room temperatue. Both **1c** (bp 78 °C/20 Torr) and **1d** (bp 80 °C/14 Torr) exhibited consistent spectral and analytical data.

5) H. Tajima, T. Masuda, and T. Higashimura, J. Polym. Sci., Polym. Chem. Ed., 25, 2033 (1987); Y. Okano, T. Masuda, and T. Higashimura, ibid., 22, 1603 (1984); M. G. Voronkov, V. B. Pukhnarevich, S. P. Sushchinskaya, V. Z. Annenkova, V. M. Annenkova, and N. J. Andreeva, ibid., 18, 53 (1980).

6) Spectral data of the prepared polymers follow. **2a:** IR (KBr) 3300 (vw), 2960, 2900, 2030 (vw), 1400, 1250, 1080, 830, 790, 660 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ = -0.2-0.8 (br m, 12 H), 2.2-2.6 (br, 0.3 H), 5.5-7.6 (br, 1.7 H); UV (CCl_4) λ_{max} 263 nm. Based on the spectral data, parts of the polymer seem to be unbridged like the structure i. **2b:** IR (KBr) 2950, 2900, 1400, 1350, 1240, 1110, 1040, 980, 950, 825, 790, 720, 680, 630 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ = -0.5-0.5 (br m, 14 H), 6.2-7.8 (br m, 2 H). **2c:** IR (KBr) 2960, 2900, 1400, 1245, 1130, 1050, 820, 770, 680, 600 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ = -0.5-1.0 (br m, 16 H), 6.0-8.0 (br, 2 H). **2d:** IR (KBr) 2970, 2900, 1410, 1260, 1060, 810, 690, 660 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ = -0.3-0.7 (br m, 18 H), 5.8-8.0 (br, 2 H). **2e:** IR (KBr) 2970, 1400, 1250, 1040, 930, 830, 780, 630 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ = -0.5-1.0 (br m, 12 H), 6.0-8.0 (br, 2 H). As the ^{1}H NMR of **2b-d** showed absorptions at the aromatic region also, the structures ii are assumed to be the real ones for **2b-d**.



i
x : y = 2-3 : 1



ii
x : y : z = 2-6 : 1 : trace

7) The doping mechanism is unclear yet, but a possible one is following. Fluoride ion interacts with organosilicon compounds to generate pentacoordinate silicate [cf. T. Hiyama, M. Obayashi, I. Mori, and H. Nozaki, J. Org. Chem., 48, 912 (1983)]. Thus, the polyene polymer turns to that which have substituent with negative charge. Upon oxidative doping, the conjugated main chain grew charged with positive charge. The zwitter ionic nature would be responsible for the conductivity.

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