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Communications to the Editor

Synthesis of Optically Active Polyacetylene Containing an Asymmetric Silicon by Using Organotransition-Metal Complexes as Catalysts

Polyacetylene, which shows metallic conductivity upon doping, has received much attention in recent years.[1] Polyacetylenes with substituents have also attracted interest among polymer scientists, and so far a number of transition-metal compounds have been found to work as effective catalysts in the polymerization of substituted acetylenes.[2] Among metal carbonyls, $M(CO)_6$ (M = Mo, W) effects the polymerization of substituted acetylenes, but UV irradiation is necessary.[3] Though many organometallic complexes can be conveniently prepared from $M(CO)_6$ by a one-pot procedure,[4] to date there are only a few reported efforts designed to employ these "simple" complexes to initiate the acetylene polymerization: $Mo(CO)_3$(toluene) induces the polymerization of $HC{\equiv}CPh$;[5] $W(CO)_4$(cycloocta-1,5-diene) at 50 °C after 7 days gives only 30% yield of poly(phenylacetylene);[2b] and $W(CO)_3$(mes)[6] was said to be a bad initiator.[5]

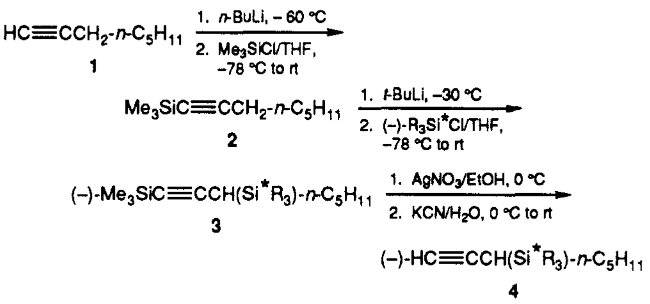
A large effort in synthetic chemistry in recent years has produced a wide range of mono- and disubstituted polyacetylenes with various pendant groups.[7] In more recent efforts in this field, the living polymerization of substituted acetylenes was achieved,[8] and the synthesis of substituted polyacetylene containing a conjugated stable polyradical was also realized.[9] However, no example is known for the synthesis of an optically active polyacetylene.

Optically active polymers are thought to be promising candidates for ferroelectric polymer liquid crystals[10] and for chiral stationary phases in the liquid chromatographic resolution of enantiomers.[11] Silicon-containing polymers are believed to have potential applications as electron-beam resists in the electronics industry.[12] Thus design of a polyacetylene containing an optically active silicon should be interesting. Here we report the synthesis of poly[(−)-3-(α-naphthylphenylmethylsilyl)-1-octyne] (**5**), an optically active polyacetylene having asymmetric silicon, by employing the simple organotransition-metal complexes $M(CO)_3(CH_3CN)_3$ and $M(CO)_3$(mes) (M = Mo, W) as catalysts.

Synthesis of the optically active monomer, (−)-3-(α-naphthylphenylmethylsilyl)-1-octyne (**4**), a new compound, was accomplished by the procedure shown in Scheme I. 1-Octyne (**1**) was converted into 1-(trimethylsilyl)-1-octyne (**2**) by treatment with *n*-BuLi followed by addition of Me_3SiCl.[13] **2** was then treated in situ with *t*-BuLi and enantiomerically pure (−)-R_3Si^*Cl,[14] prepared by a published procedure,[15] to produce the corresponding bis-silylated compound **3**. Selective desilylation of the acetylenic trimethylsilyl group in **3** was achieved with an aqueous ethanolic solution of $AgNO_3$.[13] Treatment with an aqueous solution of KCN provided **4** in satisfactory yield and with high isomeric purity.[16]

4 was polymerized in CCl_4 at 30 °C under a dry nitrogen atmosphere by $M(CO)_3(CH_3CN)_3$ (M = Mo, W)[17] complexes (Table I, nos. 1, 2).[18] In the case of $Mo(CO)_3(CH_3CN)_3$, after 24 h a polymer with a weight average molecular weight ($\bar{M}_w$) of 1×10^4 was isolated as a yellow powder in 64% yield. Optical rotation of the polymer was measured in dioxane and found to be −98°, which was about 10 times that of the monomer (−9.5°). When $W(CO)_3(CH_3CN)_3$ was used, both the yield and $\bar{M}_w$ of the polymer obtained under the same experimental conditions were low, suggesting that catalytic activity of the W complex is lower than that of the Mo complex.

Scheme I



At 30 °C, the polymerization of **4** initiated by $Mo(CO)_3$(mes)[19] was very slow. However, after 72 h at 50 °C an optically active polymer was formed in excellent yield (no. 3), indicating that this complex functioned well as catalyst at "high" temperature.

Polymerizations of **4** by "classic" WCl_6 catalysts were investigated for comparison (nos. 4, 5). Using optically pure (−)-NPMMS[20] as a cocatalyst, **4** polymerized, but the polymer yield and molecular weight were both low. Optical rotation of the polymer was also low (−86°). Optical rotation of the polymer decreased further when (+)-NPMS[20] was employed as a cocatalyst. From these results, it could be concluded that the $M(CO)_3(CH_3CN)_3$ complexes are suitable for preparing optically active polymers with high optical rotation.

Polymerizations of the racemic and achiral Si-containing acetylenes were also examined. All four racemic monomers containing asymmetric silicon and/or carbon (Table I, nos. 6–9)[21] and one achiral monomer (nos. 10, 11) failed to give optically active polymers. High polymers were nevertheless obtained in high yields (nos. 9, 10) from two monomers having trimethylsilyl group, demonstrating that the $M(CO)_3(CH_3CN)_3$ complexes are excellent initiators of acetylene polymerization. The most striking result was that $W(CO)_3$(mes)[5,19] polymerized $HC{\equiv}CC_6H_4$-*o*-$SiMe_3$ to give a very high molecular weight product, though the polymer yield was low (no. 11).

No polymers formed when polymerizations were carried out in toluene (nos. 12, 13). The same results were obtained in other non-halocarbon solvents such as cyclohexane and CH_3CN. However, high polymer ($\bar{M}_w$ 8.8×10^5) was obtained almost quantitatively (99%) when $ClC{\equiv}C$-*n*-C_6H_{13} was polymerized with $Mo(CO)_3$(mes) in toluene.[22] This suggests that the interaction of chlorine (in solvent and/or monomer) with the complex may play an important role in the formation of active species.

Structure of the optically active polymer **5** was determined by spectroscopy. Two acetylenic carbons at δ 86.42 and 70.42 (Figure 1) were observed in the ^{13}C NMR spectrum of 3-(α-naphthylphenylmethylsilyl)-1-octyne. These peaks disappeared in the spectrum of **5**. The peaks of alkyl carbons were seen in δ 0–32, and the peaks of olefinic and aromatic carbons were observed in a reasonable region. The spectrum of **5** showed no other unexpected signals. The IR spectrum of **5** showed absorptions at 3000 and 1580 cm^{-1} assignable to the $=C{-}H$ and $C{=}C$

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Table I
Polymerization of Silicon-Containing Acetylenes[a]

				polymer			
no.	monomer[b]	catalyst[c]	solvent	yield, %	$\bar{M}_w{}^d/10^3$	$\bar{M}_w/\bar{M}_n{}^d$	$[\alpha]^{25}{}_D$,[e] deg (c, g/dL)
1	$(-)$-HC$\equiv$CCH(Si*R$_3$)-n-C$_5$H$_{11}$	$Mo(CO)_3(CH_3CN)_3$	CCl_4	64	10	1.9	−98 (2.33)
2	$(-)$-HC$\equiv$CCH(Si*R$_3$)-n-C$_5$H$_{11}$	$W(CO)_3(CH_3CN)_3$	CCl_4	24	5.2	1.5	−102 (1.53)
3	$(-)$-HC$\equiv$CCH(Si*R$_3$)-n-C$_5$H$_{11}$	$Mo(CO)_3$(mes)	CCl_4	85	17	2.6	−95 (1.05)
4	$(-)$-HC$\equiv$CCH(Si*R$_3$)-n-C$_5$H$_{11}$	WCl_6-(−)-NPMMS	toluene	36	3.4	1.3	−86 (1.01)
5	$(-)$-HC$\equiv$CCH(Si*R$_3$)-n-C$_5$H$_{11}$	WCl_6-(+)-NPMS	toluene	66	8.2	2.1	−66 (1.16)
6	HC$\equiv$CCH(SiR$_3$)-n-C$_5$H$_{11}$	WCl_6	toluene	70	22	2.3	
7	R$_3$SiC$\equiv$C-n-C$_6$H$_{13}$	$Mo(CO)_3(CH_3CN)_3$	CCl_4	0			
8	HC$\equiv$CCH$_2$SiR$_3$	WCl_6-NPMS	toluene	32	9.6	5.9	
9	HC$\equiv$CCH(SiMe$_3$)-n-C$_5$H$_{11}$	$Mo(CO)_3(CH_3CN)_3$	CCl_4	88	150	2.1	
10	HC$\equiv$CC$_6$H$_4$-o-SiMe$_3$	$W(CO)_3(CH_3CN)_3$	CCl_4	100	2000	3.8	
11	HC$\equiv$CC$_6$H$_4$-o-SiMe$_3$	$W(CO)_3$(mes)	CCl_4	28	1100	3.3	
12	$(-)$-HC$\equiv$CCH(Si*R$_3$)-n-C$_5$H$_{11}$	$Mo(CO)_3(CH_3CN)_3$	toluene	0			
13	HC$\equiv$CCH(SiMe$_3$)-n-C$_5$H$_{11}$	$Mo(CO)_3(CH_3CN)_3$	toluene	0			

[a] Polymerized at 30 °C for 24 h; $[M]_0 = 0.5$ M, [Cat] = [Cocat] = 15 mM. Part of polymerization conditions were changed as follows: no. 3, at 50 °C for 72 h; no. 11, at 75 °C. [b] SiR$_3$ represents a α-naphthylphenylmethylsilyl group. [c] The mes, NPMMS, and NPMS stand for mesitylene, α-naphthylphenylmethyl-(−)-menthoxysilane, and α-naphthylphenylmethylsilane, respectively. [d] Determined by GPC on the basis of a polystyrene calibration. [e] Measured in dioxane.

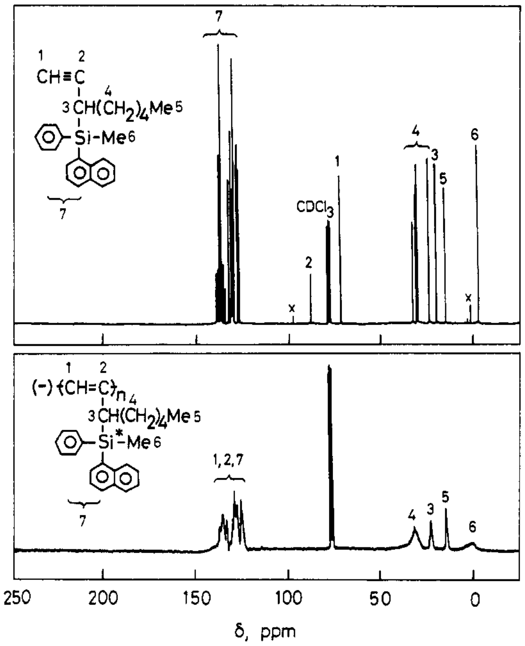

Figure 1. ^{13}C NMR spectra of the monomer and polymer of 3-(α-naphthylphenylmethylsilyl)-1-octyne (CDCl$_3$ solutions, polymer sample from Table I, no. 1).

stretching bands, respectively.[23] It therefore seems reasonable to assume that the polymer has the alternating double-bond structure shown in Figure 1.

On the basis of the above results and by taking into account that W(CO)$_3$(mes) is a catalyst for the ring-opening metathesis polymerization of cyclic olefins,[24] we propose that the present polymerization may proceed via a metal carbene machanism,[25] though further experimental evidence to support this hypothesis is needed.

Polymer **5** was totally soluble in many common organic solvents such as toluene, CHCl$_3$, THF, and dioxane. No change was recorded by differential scanning calorimetry below 250 °C, indicating that **5**, like many other substituted polyacetylenes, has a high glass transition temperature (T_g).[26] Thermogravimetric analysis showed that weight loss from **5** started at a temperature as high as 250 °C; that is to say, **5** is a thermally stable substituted polyacetylene.[27]

The present study revealed that M(CO)$_3$(CH$_3$CN)$_3$ and M(CO)$_3$(mes) (M = Mo, W) complexes effected polymerization of substituted acetylenes under mild conditions. When these complexes were employed as catalysts, an optically active substituted polyacetylene **5** with a high optical rotation was synthesized for the first time. To the best of authors' knowledge, **5** was also the first example of a polymer containing an asymmetric silicon. Since the polymer possesses a unique structure, it may have potential appication as a new specialty material. Further studies are in progress.

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Registry No. 1, 629-05-0; 2, 15719-55-8; 3, 123186-30-1; 4, 123186-29-8; 4 (homopolymer), 123186-32-3; (±)-HC$\equiv$CCH(SiMe$_3$)-n-C$_5$H$_{11}$, 123186-34-5; HC$\equiv$CC$_6$H$_4$-o-SiMe$_3$, 112754-88-8; Me$_3$SiCl, 75-77-4; (−)-R$_3$SiCl, 960-82-7; Mo(CO)$_3$(CH$_3$CN)$_3$, 15038-48-9; W(CO)$_3$(CH$_3$CN)$_3$, 16800-47-8; Mo(CO)$_3$(mes), 12089-15-5; WCl$_6$, 13283-01-7; NPMS, 1025-08-7; W(CO)$_3$(mes), 12129-69-0; R$_3$SiC$\equiv$C-n-C$_6$H$_{13}$, 123186-31-2; LiC$\equiv$C-n-C$_6$H$_{13}$, 21433-45-4; (±)-3-(α-naphthylphenylmethylsilyl)-3-propyne (homopolymer), 123284-10-6.

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(16) The overall isolated yield of 4 was 46%: colorless viscous liquid; bp 175 °C (0.68 mmHg); purity 98% (contained about 2% of the corresponding allenic isomer); $[\alpha]^{25}_{\mathrm{D}}$ –9.5° (*c* 11.05, cyclohexane). MS calcd for $C_{25}H_{28}Si$: 356.58. Found: 356.6.
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(21) (a) $R_3SiC{\equiv}C\text{-}n\text{-}C_6H_{13}$, a new compound, was synthesized by the reaction of R_3SiCl with $LiC{\equiv}C\text{-}n\text{-}C_6H_{13}$ in THF: yield 80%; colorless viscous liquid; bp 200 °C (1.5 mmHg); purity >99%. MS calcd for $C_{25}H_{28}Si$: 356.58. Found: 356.5. (b) $HC{\equiv}CCH_2SiR_3$ had previously been synthesized by Slutsky et al. from $HC{\equiv}CCH_2MgBr$ and R_3SiCl: Slutsky, J.; Kwart, H. *J. Am. Chem. Soc.* **1973**, 8678. We prepared the propargylic silane by the reaction of $HC{\equiv}CCH_2MgCl$ with R_3SiOMe: yield 70%, purity 83% (the main impurity was the corresponding allenylic silane).
(22) Polymerized at 75 °C for 24 h; details will be reported in a future paper.
(23) The further data and peak assignments of the IR spectrum of 5 were as follows: 1500, 1215, 1140, 980 (α-NpSi); 1310, 1105, 725, 705 (SiPh); 1260 (SiMe). For the peak assignments, see reference cited in note 21b.
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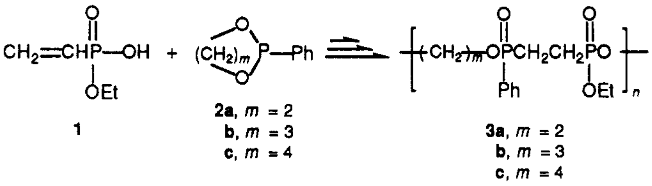
Hydrogen-Transfer Alternating Copolymerization of Vinylphosphonic Acid Monoethyl Ester with Cyclic Phosphonites. A New Oxidation–Reduction Copolymerization

In a series of studies on the alternating copolymerization via zwitterion intermediates,[1] several monomers are known to undergo a hydrogen-transfer copolymerization; the monomers have an acidic hydrogen such as acrylic acid,[2] α-keto acids,[3] and ethylenesulfonamide.[4] These reactions occur spontaneously without any added catalyst to give the corresponding 1:1 alternating copolymers.[1] The present paper reports a new copolymerization of vinylphosphonic acid monoethyl ester (1)[5] with cyclic phosphonites 2 to give alternating copolymers 3 having two kinds of phosphorus atoms in the main chain. During the copolymerization, monomer 1 was reduced involving a hydrogen-transfer process and monomer 2 was oxidized; the oxidation state of the phosphorus atom of monomer 2 is changed from trivalent to pentavalent ("oxidation–reduction copolymerization"). It is to be noted that monomer 1 has not previously been employed in the field of polymer chemistry.



When an equimolar mixture of monomer 1 and a five-, six-, or seven-membered cyclic phosphonite (**2a, 2b**, or **2c**) was heated in a solvent or bulk at 80 or 150 °C, the copolymerization occurred without catalyst to afford the corresponding copolymer 3 in good yields (Table I). The molecular weight of the resulting copolymer depends mainly upon the reaction temperature; copolymers of higher molecular weight were obtained when the reaction was carried out at 150 °C, whereas copolymers of lower molecular weight were produced at 80 °C. The copolymers of higher molecular weight are soluble in highly polar solvents such as *N,N*-dimethylformamide, methanol, and water. The copolymers of lower molecular weight are soluble not only in these solvents but also in chloroform.

The following is a typical procedure for the copolymerization betweeen 1 and **2b**: An equimolar mixture of vinylphosphonic acid monoethyl ester (1; 136 mg, 1.0 mmol) and 2-phenyl-1,3,2-dioxaphosphorinane (**2b**; 182 mg, 1.0 mmol) in benzonitrile (0.3 mL) was heated under argon at 150 °C for 90 h. After precipitation from diethyl ether, the product was dried in vacuo to give 210 mg of copolymer **3b** (66% yield).

Figure 1 shows the ^1H NMR spectrum of the copolymer obtained from 1 and **2b** at 150 °C in benzonitrile (entry