

NOTES

Polymerization of [*o*-(Dimethylphenylsilyl)phenyl]acetylene and Polymer Properties[†]

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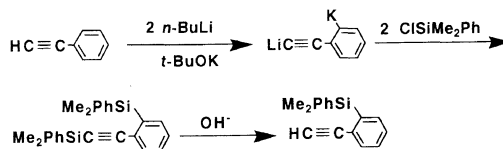
Polymerization of various *ortho*-substituted phenylacetylenes has recently been studied; e.g., *o*-methylphenylacetylene,² *o*-(trifluoromethyl)phenylacetylene,^{3,4} *o*-(trimethylsilyl)phenylacetylene (*o*-Me₃SiPA),⁵ and derivatives of *o*-Me₃SiPA.⁶ These monomers showed the following characteristics: i) they polymerize in good yields by W and Mo catalysts to form linear, soluble polymers; ii) the molecular weight of the produced polymers increases with increasing steric crowding in the monomer irrespective of the electronic effect of the substituents; iii) monomers with bulky *ortho* substituents undergo living polymerization in the presence of Mo-based three-component catalysts; iv) the absorption of polymer in the UV-visible spectrum shows a red shift as the *ortho* substituent becomes bulkier; v) the gas permeability of the polymers tends to increase with increasing bulkiness of the *ortho* substituent.

o-Me₃SiPA has the bulkiest substituent among the *ortho*-substituted phenylacetylenes whose polymerization has been examined. The above-stated characteristics are evidently seen with *o*-Me₃SiPA.⁵

It is of interest to examine whether such characteristics are strengthened or not if an even bulkier substituent is introduced into the *ortho* position of phenylacetylene. As one of such monomers we chose [*o*-(dimethylphenylsilyl)phenyl]acetylene (*o*-Me₂PhSiPA). The present paper reports on the polymerization and polymer properties of *o*-Me₂PhSiPA. The results obtained are compared with those of *o*-Me₃SiPA.

EXPERIMENTAL

o-Me₂PhSiPA (new compound) was prepared with reference to the method for *o*-Me₃SiPA.⁷



The detailed procedure is as follows: After flushed with dry nitrogen, a 1-l round-bottomed flask was equipped with a dropping funnel, a three-way stopcock, and a magnetic

[†] Part 12 of "Silicon-Containing Polyacetylenes." See ref. 1 for Part 11.

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stirring bar. A hexane solution of *n*-BuLi (390 ml, 0.63 mol) was placed in the flask, and a part of hexane (~250 ml) was evaporated with an aspirator. Tetrahydrofuran (THF; ~250 ml; dried over sodium) was added dropwise at -20°C . Then, a solution of phenylacetylene (32.9 ml, 0.30 mol) in THF (30 ml) was gradually added and the reaction mixture was left for 1 h at -10°C . After the mixture was cooled at -65°C , a solution of *t*-BuOK (33.7 g, 0.30 mol) in THF (~100 ml) was added dropwise followed by stirring at -10°C for 1 h. At -50°C ClSiMe₂Ph (104 ml, 0.63 mol) was added dropwise, and the mixture was left at room temperature overnight. After hexane and THF were evaporated, a solution of KOH (30 g) in 95% EtOH (300 ml) was added into the flask, which was stirred for 1 h at 60°C . Desilylation of the acetylenic carbon was monitored by gas chromatography (GC), and ice water (300 ml) was added after completion of the reaction. The reaction product was extracted with diethyl ether, washed with water, and dried over anhydrous sodium sulfate overnight. Diethyl ether was evaporated, and the product was purified by flush column chromatography (Nakarai Tesque Co., silica gel 60; eluent, hexane). Overall yield, 30%, purity >95% (by GC).

Transition metal chlorides and organo-metallic compounds were commercially obtained and used without further purification.

Polymerizations were carried out under dry nitrogen in a way similar to *o*-Me₃SiPA,⁵ *i.e.*, in toluene at 30°C , $[\text{M}]_0 = 0.50 \text{ M}$, and $[\text{Cat}] = [\text{Cocat}] = 20 \text{ mM}$ unless otherwise stated. Monomer conversions were determined by GC, and molecular weights of polymers were determined by gel permeation chromatography (GPC; eluent CHCl₃, polystyrene calibration).

UV-visible spectra were recorded with a Shimadzu UV-2200 spectrophotometer. Thermogravimetric analysis (TGA) was performed with a Shimadzu 20B thermal analyzer (heating rate $10^{\circ}\text{C}/\text{min}$). Gas permeability coefficients

were measured with a K-315-N gas permeability apparatus (Rikaseiki Co., Japan); membrane thickness, ~50 μm .

RESULTS AND DISCUSSION

Polymerization

Table I shows results of the polymerization by various catalysts. The WCl₆-Et₃SiH (1:1) catalyst, which is known to be very effective in the polymerization of *o*-Me₃SiPA, produced a methanol-insoluble polymer in the highest yield. The methanol-soluble products were mixture of linear oligomers and cyclotrimers. The product polymer, poly(*o*-Me₂PhSiPA), was soluble in toluene and CHCl₃, whose \bar{M}_w reached 73×10^4 . The W(CO)₆-*hν* catalyst also gave a polymer in high yield. The \bar{M}_w of the polymer exceeded 1×10^6 , being higher than that with WCl₆-Et₃SiH. When MoCl₅-Et₃SiH was used both yield and molecular weight of polymer decreased as compared with the WCl₆ counterpart. In general, both WCl₆- and MoCl₅-based catalysts are effective in the polymerization of phenylacetylene and its *ortho*-substituted derivatives, though the former is more active than the latter.⁸ This tendency holds also with *o*-Me₂PhSiPA.

NbCl₅-Et₃SiH, a catalyst based on a group 5 transition metal, also provided poly(*o*-

Table I. Polymerization of *o*-Me₂PhSiPA by various catalysts^a

Catalyst	Conversion	Polymer ^b		
	%	Yield/%	$\bar{M}_w/10^3$ ^c	$\bar{M}_n/10^3$ ^c
WCl ₆ -Et ₃ SiH	100	83	730	96
W(CO) ₆ - <i>hν</i> ^d	100	79	1300	550
MoCl ₅ -Et ₃ SiH	85	62	100	47
NbCl ₅ -Et ₃ SiH ^e	100	19	240	109
TaCl ₅ -Et ₃ SiH ^e	100	14	190	68

^a Polymerized in toluene at 30°C for 24 h; $[\text{M}]_0 = 0.50 \text{ M}$, $[\text{Cat}] = [\text{Et}_3\text{SiH}] = 10 \text{ mM}$.

^b Methanol-insoluble part.

^c Determined by GPC.

^d Polymerized in CCl₄.

^e Polymerized at 80°C .

Me₂PhSiPA) with \bar{M}_w of ca. 20×10^4 , though the polymer yield remained low. The TaCl₅-Et₃SiH catalyst also showed some activity, like NbCl₅-Et₃SiH. It is known that group 5 transition-metal chlorides selectively cyclo-trimerize most monosubstituted acetylenes. Monomers with a very bulky substituent, however, produced polymers with such catalysts [e.g., HC≡CC₆H₂-*o*,*o*-Me₂-*p*-*t*Bu,⁹ HC≡CC₆H₄-*o*-Ph]. Thus, the above results manifest that the steric effect of the *ortho* substituent of *o*-Me₂PhSiPA is considerably large.

Effects of solvents on the polymerization were studied by using WCl₆-Et₃SiH which achieved the highest polymer yield (Table II). Polymers were obtained in good yields not only in toluene but also in other solvents like hexane, (CH₂Cl)₂ and anisole. It has been noted that the polymerization by TaCl₅ does not occur in anisole, while that by WCl₆, MoCl₅, and NbCl₅ does take place in anisole. The present result corresponds to the precedents. Though the \bar{M}_w values varied depending on the solvents, they all reached several hundred thousand.

Figure 1 depicts the effect of temperature on the polymerization by WCl₆-Et₃SiH. The polymer yield is 56% at 0°C (monomer conversion is 91%), and increases to about 80% at 30°C and above. The \bar{M}_w value, which is $\sim 1 \times 10^6$ at 0°C, decreases with rising polymerization temperature. These results indicate that temperatures around 30°C are optimal to obtain a high-molecular-weight polymer in good yield.

Living Polymerization

o-Me₃SiPA undergoes living polymerization in the presence of MoOCl₄-*n*-Bu₄Sn-EtOH (1 : 1 : 1) catalyst to form a polymer with narrow molecular weight distribution (MWD; $\bar{M}_w/\bar{M}_n \sim 1.1$).¹⁰ Thus, living polymerization of *o*-Me₂PhSiPA by this catalyst was attempted. As seen in Figure 2, the number-average molecular weight of polymer (\bar{M}_n) increased in direct proportion to monomer conversion. The

Table II. Solvent effects on the polymerization of *o*-Me₂PhSiPA by WCl₆-Et₃SiH^a

Solvent	Conversion		Polymer ^b	
	%	Yield/%	$\bar{M}_w/10^{3c}$	$\bar{M}_n/10^{3c}$
Toluene	100	83	730	96
Cyclohexane	100	82	210	77
(CH ₂ Cl) ₂	85	68	900	290
Anisole	100	79	540	220

^a Polymerized at 30°C for 24 h; [M]₀ = 0.50 M, [WCl₆] = [Et₃SiH] = 10 mM.

^b Methanol-insoluble part.

^c Determined by GPC.

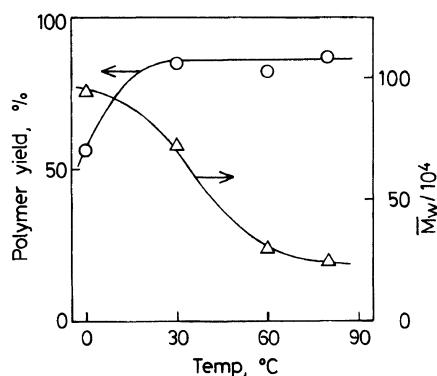


Figure 1. Effect of temperature on the polymerization of *o*-Me₂PhSiPA by WCl₆-Et₃SiH (in toluene, 24 h, [M]₀ = 0.50 M, [WCl₆] = [Et₃SiH] = 10 mM).

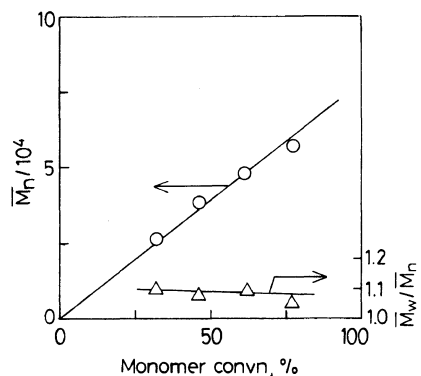


Figure 2. \bar{M}_n and \bar{M}_w/\bar{M}_n as functions of conversion in the polymerization of *o*-Me₂PhSiPA by MoOCl₄-*n*-Bu₄Sn-EtOH (in toluene, 30°C, [M]₀ = 0.50 M, [MoOCl₄] = [*n*-Bu₄Sn] = [EtOH] = 10 mM).

polymerization rate was rather slow; *i.e.*, even when *o*-Me₂PhSiPA was polymerized for 6 h, the monomer conversion was 85% and not quantitative. The MWD remained narrow ($\bar{M}_w/\bar{M}_n < 1.1$) throughout the polymerization. These results manifest that *o*-Me₂PhSiPA polymerizes in a living manner with the MoOCl₄-based three-component catalyst like *o*-Me₃SiPA. Thus, it is obvious that the *o*-dimethylphenylsilyl group, a very bulky *ortho* substituent, of phenylacetylene does not necessarily lower the livingness of its polymerization.

Polymer Properties

Since it was found that properties of poly(*o*-Me₂PhSiPA) do not depend on the polymerization conditions, those of the poly(*o*-Me₂PhSiPA) obtained by WCl₆-Et₃SiH in toluene at 30°C will be described.

Poly(*o*-Me₂PhSiPA) is a dark purple solid. It was completely soluble in aromatic hydrocarbons (toluene, benzene), chlorinated hydrocarbons (CCl₄, CHCl₃, CH₂Cl₂), and tetrahydrofuran. Its nonsolvents include aliphatic hydrocarbons (cyclohexane, hexane), ethers (anisole, diethyl ether, 1,4-dioxane), ketones (acetone, acetophenone), esters (ethyl acetate, methyl benzoate), and triethylamine. Poly(*o*-Me₃SiPA) dissolves in cyclohexane and triethylamine, which indicates that the present polymer is less soluble than poly(*o*-Me₃SiPA). A free-standing film could be prepared by casting poly(*o*-Me₂PhSiPA) from toluene solution.

The absorption maximum of poly(*o*-Me₂PhSiPA) lie at 532 nm (ϵ_{\max} 5700 M⁻¹ cm⁻¹) and the absorption extends up to *ca.* 700 nm (Figure 3). The absorption of *o*-substituted poly(phenylacetylene) shows red shifts with increasing bulkiness of substituent; *e.g.*, λ_{\max} 466 nm (*o*-CH₃),² 542 nm (*o*-SiMe₃).⁵ Absorption of poly(*o*-Me₂PhSiPA) is, however, similar in wavelength to that of poly(*o*-Me₃SiPA).

The P_{O_2} value of poly(*o*-Me₂PhSiPA) at 25°C was 4.1 barrer, being appreciably smaller

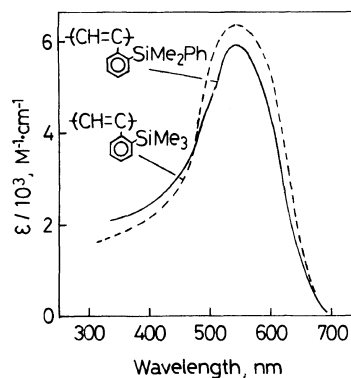


Figure 3. UV-visible spectra of poly(*o*-silylphenylacetylenes) (measured in THF).

than that of poly(*o*-Me₃SiPA) [P_{O_2} value of poly(*o*-Me₃SiPA) was 78 barrer]. Whereas poly[1-(trimethylsilyl)-1-propyne], a silicon-containing polyacetylene, shows the highest gas permeability among synthetic polymers, the gas permeability decreases when one of the methyl groups on the Si atom in the polymer is replaced by a bulkier substituent such as -CH₂SiMe₃.¹¹ Thus, the present result resembles the case of poly[1-(trimethylsilyl)-1-propyne].

CONCLUSIONS

o-Me₂PhSiPA polymerized with W catalysts in good yields to form high-molecular-weight polymers ($\bar{M}_w > 10^6$). Mo, Nb, and Ta catalysts also provided polymers, though the polymer yields and molecular weights were lower than those with WCl₆. The produced polymer was a dark purple solid soluble in various organic solvents. Gas permeability of poly(*o*-Me₂PhSiPA) was appreciably smaller than that of poly(*o*-Me₃SiPA).

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