

NOTES

Polymerization of 1-[*m*-(Trimethylsilyl)phenyl]-1-propyne and Polymer Properties

Kenji TSUCHIHARA, Tatsuya OSHITA, Toshio MASUDA,*
and Toshinobu HIGASHIMURA*

*Department of Polymer Chemistry, Kyoto University,
Kyoto 606, Japan*

(Received March 14, 1991)

KEY WORDS 1-[*m*-(Trimethylsilyl)phenyl]-1-propyne / Substituted Acetylene / Metathesis Polymerization / Transition-Metal Catalyst / Silicon-Containing Polymer / Molecular-Weight Decrease / Gas Permeability /

Silicon-containing polyacetylenes often exhibit unique properties, especially high gas permeability.^{1,2} For example, poly[1-(trimethylsilyl)-1-propyne] [poly(TMSP)] shows the highest gas permeability among all the synthetic polymers,³ and has recently been under intensive research.^{4,5} Therefore, it is of interest to introduce trimethylsilyl group into the side chain of various polyacetylenes.

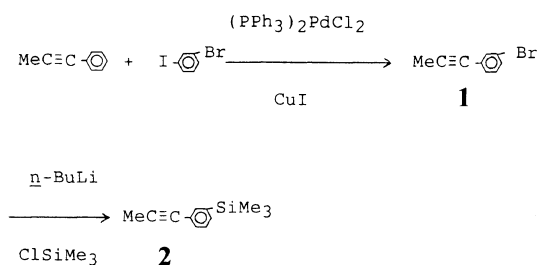
Disubstituted acetylenes are known to undergo metathesis polymerization with Nb and Ta catalysts. Among them, 1-phenyl-1-propyne⁶ (MeC≡CPh; PhP) affords a polymer having a weight-average molecular weight (\bar{M}_w) over 1×10^6 . The polymer [poly(PhP)] is a white solid, which is soluble in many organic solvents and thermally fairly stable. It is one of the least gas-permeable polyacetylenes.

The present paper reports on the polymerization of 1-[*m*-(trimethylsilyl)phenyl]-1-propyne (MeC≡CC₆H₄-*m*-SiMe₃; *m*-Me₃SiPhP), a silicon-containing PhP, and properties (especially, gas permeability) of the product polymer. We anticipated that the *o*-trimethylsilyl substituted PhP would not polymerize owing to too large a steric hindrance. Hence, the meta derivative, for which an appropriate steric effect is expected, was chosen as monomer. *m*-Me₃SiPhP polymerized with NbCl₅

to give a new, high molecular weight polymer in high yield. The polymer showed oxygen permeability (P_{O_2} 40×10^{-10} cm³ (STP)·cm·cm⁻²·s⁻¹·cmHg⁻¹) higher than that of poly(PhP) (P_{O_2} = 6.3×10^{-10} cm³ (STP)·cm·cm⁻²·s⁻¹·cmHg⁻¹). The polymerization behavior and polymer properties of *m*-Me₃SiPhP are compared with those of PhP.

EXPERIMENTAL

The monomer, *m*-Me₃SiPhP, was prepared according to the following scheme with reference to the method of T.-L. Chang *et al.*⁷



1-(*m*-Bromophenyl)-1-propyne (1)

After flushed with nitrogen, a 500-ml flask was charged with dry triethylamine (150 ml), (Ph₃P)₂PdCl₂ (0.84 g, 1.2 mmol), Ph₃P (1.3 g, 1.8 mmol), CuI (1.4 g, 7.2 mmol), and 1-bromo-

3-iodobenzene (15.3 ml, 0.12 mol). Then, propyne (4.5 ml, 0.24 mol) was bubbled for 5 min into the mixture at 10°C, and the mixture was stirred for 1 h at room temperature. The completion of the reaction was confirmed by gas chromatography (GC), and triethylamine was evaporated. Diethyl ether (200 ml) was added, and insoluble salts were filtered off. The solution was washed with 5% hydrochloric acid and water. The organic phase was dried over anhydrous sodium sulfate overnight, ether was evaporated, and the product was distilled at reduced pressure; bp 90–92°C/3 mmHg, yield 60%, d_4^{20} 1.384.

m-Me₃SiPhP (2)

A 200-ml flask was flushed with dry nitrogen, and charged with a hexane solution of *n*-butyllithium (62.5 ml, 1.6 M, 0.10 mol). Part of the hexane (*ca.* 40 ml) was evaporated with an aspirator under magnetic stirring. After the flask was cooled at –20°C, diethyl ether (30 ml; dried over sodium) was gradually added at the same temperature, a solution of **1** (14.1 ml, 0.10 mol) in ether (10 ml) was added dropwise, and the reaction mixture was left for 30 min. Chlorotrimethylsilane (12.7 ml, 0.10 mol) was gradually added at –20°C, and the mixture was allowed to stand at room temperature for 1 h. After the completion of the reaction had been confirmed by GC, ice water (50 ml) was added. The product was extracted with diethyl ether, washed with water, and dried over anhydrous sodium sulfate overnight. Diethyl ether was evaporated, and the product was distilled twice at reduced pressure from calcium hydride: bp 95°C/3 mmHg, yield 45%, purity >99% (by GC); d_4^{20} 0.899.

Transition metal chlorides and organometallic cocatalysts were commercially obtained and used without further purification. Polymerizations were carried out under dry nitrogen in a way similar to PhP,⁶ *i.e.*, in toluene at 80°C, [M]₀ = 0.50 M, [Cat] = [Cocat] = 10 mM unless otherwise stated. Monomer conversions were determined by GC, and mo-

lecular weights of polymers were determined by GPC (eluent, CHCl₃) with use of a polystyrene calibration.

UV-visible spectra were recorded with a Shimadzu UV 190 spectrophotometer. Thermogravimetric analysis (TGA) was performed with a Shimadzu 20B thermal analyzer (heating rate 10°C min⁻¹). 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 for the polymerization of *m*-Me₃SiPhP by TaCl₅- and NbCl₅-based catalysts. When *m*-Me₃SiPhP was polymerized with NbCl₅ alone, this monomer was completely consumed to give a methanol-insoluble polymer in high yield. The weight-average

Table I. Polymerization of *m*-Me₃SiPhP by various Nb and Ta catalysts^a

Cocat	Conversion	Polymer ^b		
	%	Yield/%	$\bar{M}_w/10^3$ ^c	$\bar{M}_n/10^3$ ^c
NbCl ₅ -cocatalyst				
none	100	89	680	72
<i>n</i> Bu ₄ Sn	100	91 ^d	—	—
Ph ₄ Sn	100	93 ^d	—	—
Et ₃ SiH	100	83 ^d	—	—
Ph ₃ SiH	100	85 ^d	—	—
Ph ₃ Sb	100	100 ^d	—	—
Ph ₃ Bi	100	97 ^d	—	—
TaCl ₅ -cocatalyst				
none	53	23	140	42
<i>n</i> Bu ₄ Sn	100	68 ^d	—	—
Ph ₄ Sn	100	49	1000	170
Et ₃ SiH	79	52	220	56
Ph ₃ SiH	100	46	120	18
Ph ₃ Sb	60	38	350	170
Ph ₃ Bi	71	42	890	260

^a Polymerized in toluene at 80°C for 24 h; [M]₀ = 0.50 M, [Cat] = [Cocat] = 10 mM.

^b MeOH-insoluble part.

^c Determined by GPC.

^d Partly insoluble in CHCl₃.

molecular weight (\bar{M}_w) of the polymer reached 680×10^3 , but the molecular weight distribution was broad. When organometallic cocatalysts, which are effective for the polymerization of PhP, were used in conjunction with NbCl_5 , polymers were formed in high yields as well. The polymers were, however, partly insoluble in CHCl_3 . The tendency that NbCl_5 -cocatalyst systems produce insoluble polymers has been observed with 1-(trimethylsilyl)-1-propyne as well.⁸ This is probably because NbCl_5 provide polymers having relatively high stereoregularity⁹ and further the use of a cocatalyst increases its molecular weight.

When TaCl_5 alone was used as catalyst, the monomer conversion did not reach 100%, and the polymer yield was considerably lower than that for NbCl_5 . Use of cocatalysts for TaCl_5 was more or less effective in the increase of yield and \bar{M}_w of polymer. NbCl_5 alone, however, achieves a higher polymer yield than do these TaCl_5 -cocatalyst systems. The differences between monomer conversion and polymer yield were due to the formation of cyclotrimers.

When PhP is polymerized with NbCl_5 or TaCl_5 alone, the molecular weight of the polymer formed decreases after complete consumption of monomer.⁶ It is interesting whether this molecular weight decrease is prevented by the introduction of the bulky trimethylsilyl group into meta position. Thus, time course of the polymerization was studied using the NbCl_5 catalyst which achieves a high polymer yield (Figure 1). The monomer conversion reached 100% after 6 h. The reaction rate is smaller than that of PhP (the polymerization of PhP proceeded completely within 2 h). The \bar{M}_w of polymer was $\sim 600 \times 10^3$ after 6 h, which was maintained even after 24 h. Thus, it is possible to restrain the decrease of molecular weight by increasing bulkiness of the substituent.

As seen in Figure 1, the \bar{M}_w of polymer increased approximately in proportion to monomer conversion. This indicates the presence

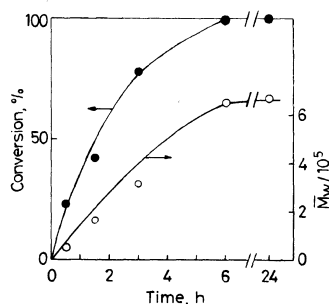


Figure 1. Time course of the polymerization of *m*- Me_3SiPhP by NbCl_5 (in toluene, 80°C; $[\text{M}]_0 = 0.50 \text{ M}$; $[\text{NbCl}_5] = 10 \text{ mM}$).

Table II. Solvent effects on the polymerization of *m*- Me_3SiPhP by NbCl_5 ^a

Solvent	Conversion		Polymer ^b	
	%	Yield/%	$\bar{M}_w / 10^3$ ^c	$\bar{M}_n / 10^3$ ^c
Toluene	100	89	680	72
Heptane	100	75 ^d	—	—
CCl_4	66	37	100	30
$(\text{CH}_2\text{Cl})_2$	100	73	440	93
Anisole	100	72	360	88

^a Polymerized in toluene at 80°C for 24 h; $[\text{M}]_0 = 0.50 \text{ M}$, $[\text{NbCl}_5] = 10 \text{ mM}$.

^b MeOH-insoluble part.

^c Determined by GPC.

^d Partly insoluble in CHCl_3 .

of a long-lived propagating species. Such a tendency was seen also in the polymerization of 1-phenyl-1-alkynes by NbCl_5 and TaCl_5 .⁶

Solvent effects on the polymerization by NbCl_5 were studied (Table II). High-molecular-weight polymers were obtained in good yields not only in hydrocarbon solvents but also in chlorine-containing solvents and anisole.

In order to know the relative monomer reactivity in the propagation reaction, copolymerization of *m*- Me_3SiPhP with PhP was attempted in toluene solution at 80°C; $[\text{M}_1]_0 = [\text{M}_2]_0 = 0.25 \text{ M}$, $[\text{NbCl}_5] = 20 \text{ mM}$. Both monomers reacted virtually at the same rate (relative rate, *m*- Me_3SiPhP : PhP = 0.9: 1). Further, *m*- Me_3SiPhP was more reactive than

1-(*m*-bromophenyl)-1-propyne (*m*-BrPhP) in their copolymerization (relative rate, *m*-Me₃SiPhP : *m*-BrPhP = 2 : 1). In general, the relative monomer reactivity in copolymerization is determined by steric and electronic effects; *i.e.*, it increases with decreasing bulkiness of substituent and with increasing electron-donating ability of substituent.^{10,11} Consequently, the similar reactivities of PhP and *m*-Me₃SiPhP are attributable to compensation of the steric and electronic effects in the latter monomer.

Structure and Properties of the Polymer

The structure and properties were studied by using the poly(*m*-Me₃SiPhP) obtained with NbCl₅ alone in Table I.

The elemental analysis values for the polymer agreed well with the ones calculated for the polymerization product; *Anal.* Calcd for (C₁₂H₁₆Si)_n: C, 76.6%; H, 8.5%; Si, 14.9%; Found: C, 76.9%; H, 8.3%; Si, 14.9%.

The IR spectrum of poly(*m*-Me₃SiPhP) showed no signal characteristic of the C≡C stretching (2200 cm⁻¹) seen in the monomer. Instead, an absorption assignable to the C=C stretching appeared at ~1580 cm⁻¹ (w). Furthermore, no signals due to acetylenic carbons were observed in the ¹³C NMR spectrum of poly(*m*-Me₃SiPhP). These analytical and spectral data are compatible with the polymer structure of -(CMe=CC₆H₄-*m*-SiMe₃)_n.

Poly(*m*-Me₃SiPhP) is a novel polymer with the form of white solid. The solubility of the polymer is as follows: completely soluble in toluene, cyclohexane, CCl₄, CHCl₃ and anisole; partly soluble in *n*-hexane, diethyl ether and tetrahydrofuran; and insoluble in (CH₂Cl)₂, 1,4-dioxane, acetone, acetophenone, ethyl acetate, methyl benzoate, nitrobenzene, and acetonitrile. A tough film could be obtained by casting the polymer from toluene solution.

Figure 2 shows UV-visible spectra of poly(*m*-Me₃SiPhP) and poly(PhP). The ab-

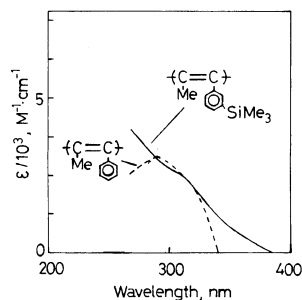
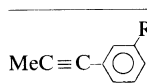


Figure 2. UV-visible spectra of poly(1-phenyl-1-propynes) (measured in cyclohexane).

Table III. Gas permeability of poly(1-phenyl-1-propynes)

	<i>P</i> ^a					
	He	H ₂	O ₂	N ₂	CO ₂	CH ₄
SiMe ₃	105	159	40	13	120	25
H ^b	30	43	6.3	2.2	25	2.8

^a Gas permeability coefficient in the units of 1×10^{-10} cm³ (STP) · cm / (cm² · s · cmHg) at 25°C.

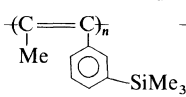
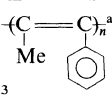
^b Data from ref 10.

sorption of poly(*m*-Me₃SiPhP) appears only below 400 nm, *i.e.*, in the ultraviolet region, which corresponds to the fact that poly(*m*-Me₃SiPhP) is a white solid. The absorption pattern resemble that of poly(PhP), although a minor difference is seen in the 350–400 nm region.

In the TGA measurement in air, poly(*m*-Me₃SiPhP) began to lose weight at 310°C, whereas poly(PhP) did at 280°C; *i.e.*, introduction of trimethylsilyl group somewhat increased thermal stability. Even after the poly(*m*-Me₃SiPhP) had been heated at 120°C for 20 h in air, no molecular-weight change was observed. Thus, poly(*m*-Me₃SiPhP) turns out thermally fairly stable among substituted polyacetylenes.

The gas permeability of a poly(*m*-Me₃SiPhP) membrane was studied by using the polymer sample with the highest molecular weight (cat: TaCl₅-Ph₃Bi). The permeability coefficients of

Table IV. Comparison of poly(*m*-Me₃SiPhP) with poly(PhP)

		
Polymer degradn ^b	No	Yes
$\bar{M}_w/10^3$	1000	1800
$T_0, ^\circ\text{C}^c$	310	280
$P_{\text{O}_2}^d$	40	6.3

^a Data from ref 6 and 10.

^b Molecular-weight decrease after the polymerization by NbCl₅ or TaCl₅ is completed.

^c Temperature at which weight loss starts in air.

^d Oxygen permeability coefficient in the units of $1 \times 10^{-10} \text{ cm}^3 \text{ (STP)} \cdot \text{cm} / (\text{cm}^2 \cdot \text{s} \cdot \text{cmHg})$ at 25°C.

poly(*m*-Me₃SiPhP) were 3–10 times as large as those of poly(PhP) for all the gases examined (Table III). Thus, gas permeability is enhanced by the introduction of trimethylsilyl group. The gas permeability of poly(*m*-Me₃SiPhP), however, is medium among those of various substituted polyacetylenes.¹²

Comparison with PhP

In Table IV, the polymerization behavior and polymer properties of *m*-Me₃SiPhP are compared with those of PhP:

i) In the polymerization of PhP by NbCl₅ and TaCl₅, the molecular weight of polymer decreases after the monomer has been completely consumed. In contrast, no decrease in molecular weight occurred in the case of *m*-Me₃SiPhP. This is explained by an idea that the bulky trimethylsilyl group inhibits the attack (back-biting) of the main chain by the propagating species.

ii) The molecular weight of poly(*m*-Me₃-SiPhP) reached 1×10^6 , which is slightly lower than that of poly(PhP). Thus, trimethylsilyl group at meta position of PhP does not affect very much the molecular weight of the polymer formed.

iii) Though poly(*m*-Me₃SiPhP)s obtained with NbCl₅ alone and TaCl₅-cocatalyst systems were soluble in various organic solvents,

the polymers formed with NbCl₅-cocatalyst systems were insoluble. In contrast, poly(PhP) is soluble in many organic solvents irrespective of the kind of catalyst. This difference seems due to the lower flexibility of the more sterically crowded poly(*m*-Me₃SiPhP).

iv) The thermal stability of poly(*m*-Me₃-SiPhP) did not greatly differ from that of poly(PhP). It is, however, noted that these polymers are thermally more stable than sterically less crowded polymers such as poly(2-alkynes).

v) Poly(PhP) is one of the substituted polyacetylenes that show the lowest gas permeability.¹² The oxygen permeability coefficient of poly(*m*-Me₃SiPhP) was one order of magnitude larger than that of poly(PhP). This conforms with the general tendency that silicon-containing polyacetylenes exhibit high oxygen permeability.

Acknowledgment. We thank Dr. K. Tamao for helpful discussions on monomer synthesis. This research was partly supported by the Grant-in-Aid for Scientific Research on Priority Areas "New Functionality Materials" from the Ministry of Education, Science, and Culture of Japan.

REFERENCES

1. T. Masuda and T. Higashimura, *Adv. Chem. Ser.*, No. **224**, (1990), Chapter 35.
2. G. Costa, in "Comprehensive Polymer Science," Vol. 4, G. Allen, Ed., Pergamon, New York, 1989, Chapter 9.
3. T. Masuda, E. Isobe, T. Higashimura, and K. Takada, *J. Am. Chem. Soc.*, **105**, 7473 (1983).
4. Y. Ichiraku, S. A. Stern, and T. Nakagawa, *J. Membrane Sci.*, **34**, 5 (1987).
5. M. Langsam, M. Anand, and E. J. Karwacki, *Gas Sep. Purification*, **2**, 3 (1988).
6. T. Masuda, T. Takahashi, and T. Higashimura, *Macromolecules*, **18**, 312 (1985).
7. T.-L. Chang, L. J. Holzknicht, H. B. Mark, Jr., T. H. Ridgway, and H. Zimmer, *J. Polym. Sci., A, Polym. Chem. Ed.*, **27**, 989 (1989).
8. T. Masuda, E. Isobe, T. Hamano, and T. Higashimura, *Macromolecules*, **19**, 2448 (1986).

9. H. Izumikawa, T. Masuda, and T. Higashimura, *Polym. Bull.*, in press.
10. K. Hasegawa, T. Masuda, and T. Higashimura, *Macromolecules*, **8**, 255 (1975).
11. T. Hamano, T. Masuda, and T. Higashimura, *J. Polym. Sci., A, Polym. Chem. Ed.*, **26**, 2603 (1988).
12. T. Masuda, Y. Iguchi, B.-Z. Tang, and T. Higashimura, *Polymer*, **29**, 2041 (1988).