

## 폴리(1-페닐-2-트리메틸실릴아세틸렌)의 합성과 특성

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## Synthesis and Properties of Poly(1-phenyl-2-trimethyl-silylacetylene)

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**요약 :** 여러가지 전이금속 촉매에 의해서 1-페닐-2-트리메틸실릴아세틸렌을 중합시킨 결과  $WCl_6$ 에 대한 단량체의 몰비와  $WCl_6$ 에 대한  $Me_4Sn$ 의 몰비가 각각 50과 1일때 가장 좋은 중합수율을 보였다. NMR, IR, UV-Visible 스펙트라등을 분석한 결과 합성한 중합체는 어느 정도 트리메틸실릴기가 떨어진 부분을 포함하는 선형 공액구조의 중합체임을 알 수 있었다. 이 중합체는 할로로포름, 벤젠, 사염화탄소와 같은 방향성 혹은 할로젠화 탄화수소 용매에 완전히 용해하였다. THF 용매에서  $(n-Bu)_4N^+F^-$ 에 의한 폴리(1-페닐-2-트리메틸실릴아세틸렌)의 디실릴레이션 반응결과 실릴기가 없는 폴리(페닐아세틸렌)를 합성할 수 있었다.

**Abstract :** The polymerization of 1-phenyl-2-trimethylsilylacetylene was carried out using various transition metal catalysts. The best result was obtained when the mole ratios of monomer to  $WCl_6$  and  $Me_4Sn$  to  $WCl_6$  were 50 and 1, respectively.  $WCl_6$ -based catalysts were more effective than  $MoCl_5$ -based catalysts. The NMR, IR, and UV-visible spectra indicated that the resulting polymer has a linear conjugated polyene containing some desilylated portion. This polymer is completely soluble in aromatic and halogenated hydrocarbons such as chloroform, benzene,  $CCl_4$ , etc. The desilylation reaction of poly(1-phenyl-2-trimethylsilylacetylene) by  $(n-Bu)_4N^+F^-$  in THF gives a completely desilylated one, i. e. poly(phenylacetylene).

### INTRODUCTION

There have been many studies on the polymerization of acetylene and substituted acetylenes with Ziegler catalysts.<sup>1~4</sup> To our knowledge, however, Ziegler catalysts such as  $Fe(acac)_3-Et_3Al$  and  $Ti(O-n-Bu)_4-Et_3Al$  do not polymerize disubstituted acet-

ylenes.<sup>5</sup> Halides of niobium(Nb) and tantalum(Ta), group 5 transition metals, are known to selectively cyclotrimerize acetylene and monosubstituted acetylenes(phenylacetylene, 1-hexyne).<sup>6,7</sup> On the other hand, it has been reported that simple pentachlorides of Nb and Ta polymerize disubstituted acetylenes(1-phenyl-1-propyne, 2,3,4-octyne).<sup>8</sup>

It was found that organoaluminum compounds ( $\text{EtAlCl}_2$ ,  $\text{Et}_2\text{AlCl}$ ) were effective cocatalysts for the polymerization of 1-chloro-2-thienylacetylene<sup>9</sup> and cyclopolymerization of nonconjugated diynes<sup>11-14</sup> by  $\text{WCl}_6$  and  $\text{MoCl}_5$ . In recent years, it was reported that 1-(trimethylsilyl)-1-propyne(TMSP), which is a Si-containing disubstituted acetylene, was polymerized by  $\text{TaCl}_5$  to produce a new high molecular weight polymer in high yields,<sup>15</sup> and that the polymer shows extremely high oxygen permeability.<sup>16-19</sup> The permeability coefficient(P) of this polymer for oxygen reaches  $\sim 10$  times the value for poly(dimethylsiloxane), which was previously known to have the largest P value among all the existing polymers.

In our previous paper,<sup>20</sup> we briefly reported the polymerization of 1-phenyl-2-trimethylsilylacetylene(PTSA) by transition metal catalysts. This article describes the full accounts for the polymerization of PTSA by various transition metal catalysts, and the characterization and physical properties of the resulting poly(1-phenyl-2-trimethylsilylacetylene)[PPTSA].

## EXPERIMENTAL

### Materials

Phenylacetylene(Aldrich Chemicals, 98%) was dried over calcium hydride and fractionally distilled at reduced pressure. *n*-Butyllithium(Aldrich Chemicals, 2.5 M solution in hexanes) was used as received. Tungsten(VI) and molybdenum(V) chlorides(Aldrich Chemicals, resublimed, 99+ %) were used without further purification. Tetraphenyltin(Aldrich Chemicals, 97%) was purified by recrystallization twice from carbon tetrachloride. Tetra-*n*-butyltin, tetramethyltin, and organoaluminum compounds were used as received. Solvents for the polymerization were all analytical grade materials. They were dried and fractionally distilled.

### Instruments

$^1\text{H}$ -NMR spectra were recorded on a Varian T-60A spectrometer and Varian FT T-80A spectrometer( $\delta$  value from TMS standard).<sup>13</sup> C-NMR

spectra were taken on a Bruker AM-200 spectrometer(50.32 MHz). Infrared spectra were taken on a Perkin-Elmer, Model 267 grating spectrometer using a potassium bromide pellets or sodium chloride disks. Ultraviolet-visible spectra were obtained with a Cary 17 spectrophotometer. Ultraviolet irradiation of  $\text{M}(\text{CO})_6(\text{M}=\text{W}, \text{Mo}, \text{Cr})$  in  $\text{CCl}_4$  was performed with 200W a high pressure mercury lamp(Model 440W absorbance detector fixed at 350 nm). The average molecular weights of the polymers were measured by means of GPC-150C of Waters using a calibration curves for polystyrene. Thermogravimetric analysis (TGA) were performed under nitrogen atmosphere at a heating rate of  $10^\circ\text{C}/\text{min}$ . up to  $600^\circ\text{C}$ . Thermal transitions were measured with a Dupont 910 differential scanning calorimeter(DSC) under nitrogen atmosphere at a heating rate of  $10^\circ\text{C}/\text{min}$ . X-ray diffraction analyses were performed on JEOL X-ray diffractometer with Cu-K $\alpha$  radiation at a scan speed of  $4^\circ/\text{min}$ .

### Preparation of PTSA

In a 500ml flask, equipped with magnetic stirrer, reflux condenser, additional funnel, and protected by an purified nitrogen atmosphere were placed 30 g(0.294 mole) of phenylacetylene and 150ml of ethyl ether. Over a one hour, 120ml of 2.5M *n*-butyllithium(0.30 mole, in hexanes) was added to the reaction solution. Then, 39g(0.36 mole) of trimethylsilylchloride was added over a 15 min, and the mixture was refluxed overnight. The mixture then was filtered through a sintered glass filter to remove the precipitated lithium chloride, and the ether was removed by rotary evaporator. Fractional distillation of the residue gave 35.9g of PTSA. Yield : 70 %, bp  $65^\circ\text{C}/1.5 \text{ mmHg}(\text{lit.}^{21} \text{ } 59\sim 60^\circ\text{C}/1.0 \text{ mmHg})$ .

$^1\text{H}$ -NMR(Fig. 1, neat, external TMS standard,  $\delta$  ppm) 0.2(9H), 7.08-7.53(5H)

$^{13}\text{C}$ -NMR(Fig. 2,  $\delta$ , ppm) 94, 105.28, 123.29, 128.19, 128.44, 131.95

IR(Fig. 3, KBr pellet,  $\text{cm}^{-1}$ ) 3080(m), 3100(m), 2180(s), 1610(w), 840(vs), 870(vs).

### Preparation of Catalyst Systems

All procedures for catalyst system preparation were carried out under dry nitrogen atmosphere because the active species are sensitive to moisture or oxygen. Transition metal chlorides and organoaluminum compounds were dissolved in chlorobenzene as 0.2 M and 0.05 M solutions before use. Tantalum(V) and niobium(V) halide, and  $M(\text{CO})_6$  ( $M = \text{W}, \text{Mo}, \text{Cr}$ ) were added as a powder in each polymerization solvents.

### Polymerization Procedures

The examples of polymerization procedure are described below. The resulting polymers were dissolved in chloroform followed by precipitation into excess methanol. The precipitated polymers were filtered from the solution and dried to constant weight under vacuum at 40°C for 24 h. The polymer yield was calculated by gravimetry.

### Polymerization by $\text{WCl}_6$ - $\text{Me}_4\text{Sn}$

A catalyst solution was prepared by mixing  $\text{WCl}_6$  (0.575 ml 0.2 M chlorobenzene solution,  $1.15 \times 10^{-4}$  mol) and  $\text{Me}_4\text{Sn}$  (0.575 ml 0.2 M chlorobenzene solution,  $1.15 \times 10^{-4}$  mol) and chlorobenzene (0.72 ml,  $[\text{M}]_0 = 2\text{M}$ ) and aged by keeping at 30°C for 5 min. To this solution was added PTSA (1g,  $5.7 \times 10^{-3}$  mol). The polymerization was carried out at 80°C for 24

hrs and terminated with a small amount of methanol. Polymer yield 33%.

### Polymerization by $\text{TaCl}_5$

$\text{TaCl}_5$  (0.068g,  $1.90 \times 10^{-4}$  mol) was dissolved in chlorobenzene (4.23 ml). To this catalyst solution, PTSA (1g,  $5.7 \times 10^{-3}$  mol), was added at 80°C. Polymerization was stopped after 24 hrs. Polymer yield 10%.

### Polymerization by $\text{W}(\text{CO})_6$ - $\text{CCl}_4$ -hv

A catalyst solution of  $\text{W}(\text{CO})_6$  (0.04g,  $1.14 \times 10^{-4}$  mol) in  $\text{CCl}_4$  (10.6 ml) was irradiated with UV light at 30°C for 1 hr. To this solution was added PTSA (1g,  $5.75 \times 10^{-3}$  mol), and polymerization was run in the dark at 60°C for 24 hrs. Polymer yield 7%.

## RESULTS AND DISCUSSION

### Polymerization

The polymerization of PTSA, silicon-containing disubstituted acetylene, was carried out by various transition metal catalysts. Table 1 shows the results for the polymerization of PTSA by  $\text{WCl}_6$ -based catalysts under various reaction conditions.

As shown in this table (Exp. No. 1-3), the polymer yield was also increased as the initial monomer concentration ( $[\text{M}]_0$ ) is increased. The

**Table 1.** Polymerization of 1-Phenyl-2-Trimethylsilylacetylene by  $\text{WCl}_6$ -Based Catalysts<sup>a</sup>

Exp. No.	Catalyst System (mole ratio)	$[\text{M}]_0$	M/C <sup>b</sup> (mole ratio)	P.Y. <sup>c</sup> (%)
1	$\text{WCl}_6$	1	50	25
2	$\text{WCl}_6$	0.5	50	15
3	$\text{WCl}_6$	2	50	26
4	$\text{WCl}_6$ - $\text{Me}_4\text{Sn}$ (1 : 1)	2	50	33
5	$\text{WCl}_6$ - $\text{Me}_4\text{Sn}$ (1 : 1)	2	100	15
6	$\text{WCl}_6$ - $\text{Me}_4\text{Sn}$ (1 : 1)	2	200	trace
7	$\text{WCl}_6$ - $n\text{-Bu}_4\text{Sn}$ (1 : 1)	2	50	30
8	$\text{WCl}_6$ - $\text{Ph}_4\text{Sn}$ (1 : 1)	2	50	31
9	$\text{WCl}_6$ - $\text{Et}_3\text{Al}$ (1 : 2)	2	50	3
10	$\text{WCl}_6$ - $\text{Et}_2\text{AlCl}$ (1 : 2)	2	50	5

<sup>a</sup>Polymerization was carried out at 80°C for 24 h in chlorobenzene.

<sup>b</sup>Mole ratio of monomer to catalyst.

<sup>c</sup>Methanol-insoluble polymer.

polymer yield was found to be strongly dependent on the mole ratio of PTSA to catalyst(Exp. No. 4-6). When the mole ratio of PTSA to catalyst was 200, the activity of this catalyst was shown to be very low.

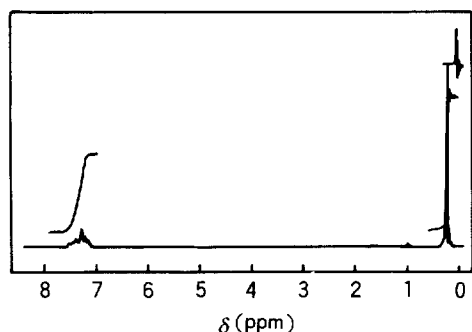


Fig. 1.  $^1\text{H}$ -NMR spectrum of 1-phenyl-2-trimethylsilylacetylene.

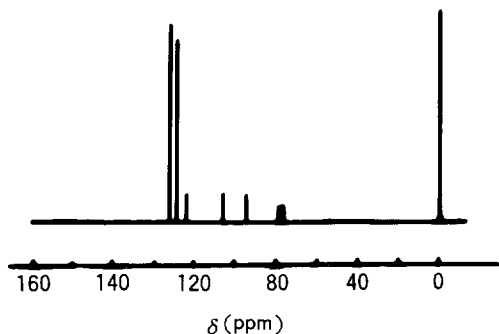


Fig. 2.  $^{13}\text{C}$ -NMR spectrum of 1-phenyl-2-trimethylsilylacetylene(solvent :  $\text{CDCl}_3$ ).

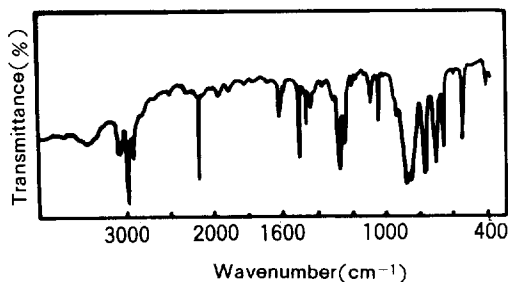


Fig. 3. IR spectrum of 1-phenyl-2-trimethylsilylacetylene.

$\text{WCl}_6\text{-R}_4\text{Sn}$ ( $\text{R}=\text{Me}$ ,  $n\text{-Bu}$ ,  $\text{Ph}$ ) catalyst systems polymerize PTSA to yield a considerable amount of methanol-insoluble polymer. The best result (polymer yield 33%) was obtained when the mole ratios of PTSA to  $\text{WCl}_6$  and  $\text{Me}_4\text{Sn}$  to  $\text{WCl}_6$  were 50 and 1, respectively. The polymerization was decelerated when a organoaluminum compounds such as  $\text{Et}_3\text{Al}$  and  $\text{Et}_2\text{AlCl}$  are used as a cocatalyst. This deactivation of  $\text{WCl}_6$  by organoaluminum compounds was also observed in the polymerization of monosubstituted acetylenes such as 2-ethynylthiophene<sup>22</sup> and 2-ethynylfuran.<sup>23</sup>

Table 2 shows the temperature effects for the polymerization of PTSA by  $\text{WCl}_6\text{-Me}_4\text{Sn}$ (1 : 1). The best result was obtained when the polymerization temperature is  $80^\circ\text{C}$ .

Fig. 4 shows the increase of polymer yield on time at the polymerization of PTSA by  $\text{WCl}_6\text{-Me}_4\text{Sn}$ (1 : 1). The polymerization rate was smaller than that of other mono and di-substituted acetylenes.

Fig. 5 shows the effect of catalyst aging time after mixing  $\text{WCl}_6$  and  $\text{Me}_4\text{Sn}$ . The polymer yield reached the maximum when the aging time was 5 min. And then, the polymer yields were decreased to some lower levels with an increase in aging time.

Fig. 6 shows influence of mole ratio of  $\text{Me}_4\text{Sn}$  to  $\text{WCl}_6$  for the polymerization of PTSA. The maximum polymer yield was obtained when the mole

Table 2. Temperature Effects for the polymerization of 1-Phenyl-2-Trimethylsilylacetylene by  $\text{WCl}_6\text{-Me}_4\text{Sn}$  (1 : 1)<sup>a</sup>

Temperature( $^\circ\text{C}$ )	P. Y. (%)
30	trace
60	19
80	33
100	31
130	23

<sup>a</sup>Polymerization was carried out at  $20^\circ\text{C}$  for 24 h. Initial monomer concentration ( $[\text{M}]_0$ ) was 2M, and monomer to catalyst mole ration was 50.

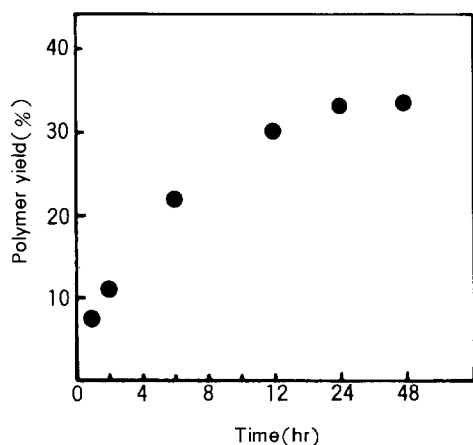


Fig. 4. Change of polymer yield on time at the polymerization of PTSA by WCl<sub>6</sub>-Me<sub>4</sub>Sn(1 : 1).

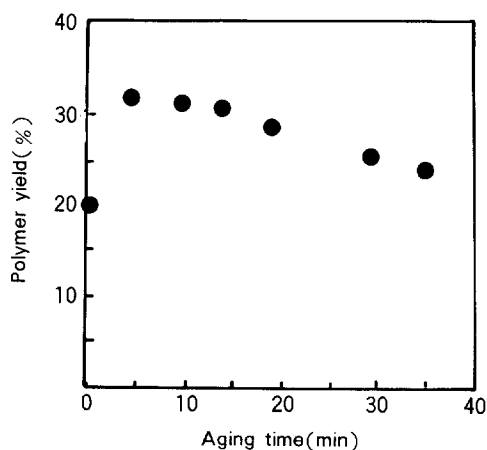


Fig. 5. Aging time effect after mixing WCl<sub>6</sub> and Me<sub>4</sub>Sn solution in the polymerization of 1-phenyl-2-trimethylsilylacetylene.

ratio of Me<sub>4</sub>Sn to WCl<sub>6</sub> is 1.

Table 3 shows the results for the polymerization of PTSA by MoCl<sub>5</sub>-Based catalysts. In general, MoCl<sub>5</sub>-based catalysts were less effective than WCl<sub>6</sub>-based catalysts as the polymer yields were very low. Ph<sub>4</sub>Sn was found to be the most effective cocatalyst among the MoCl<sub>5</sub>-based catalysts. Organoaluminum compounds did not exhibit any catalytic activity.

Table 4 shows the results for the polymerization

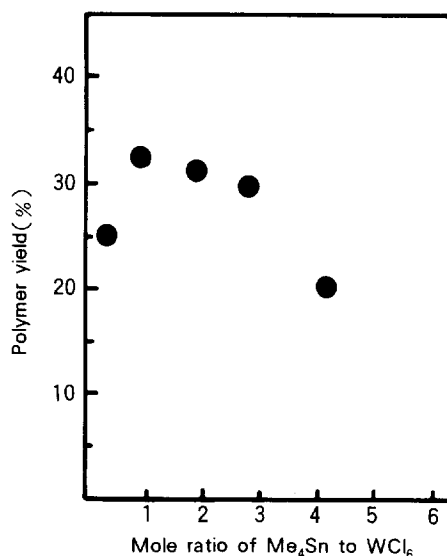


Fig. 6. Effect of mole ratio of Me<sub>4</sub>Sn to WCl<sub>6</sub> for the polymerization of 1-phenyl-2-trimethylsilylacetylene.

of PTSA by Ta and Nb halides and metal carbonyls. Ta and Nb halides which were very effective for the polymerization of some disubstituted acetylenes<sup>15</sup> were less effective for the polymerization of PTSA than WCl<sub>6</sub> alone. The polymerization of PTSA by M(CO)<sub>6</sub>-CCl<sub>4</sub>-hν was carried out at 60°C (Exp. No. 6-8). W(CO)<sub>6</sub>-CCl<sub>4</sub>-hν showed some activity, whereas Mo(CO)<sub>6</sub>-CCl<sub>4</sub>-hν and Cr(CO)<sub>6</sub>-CCl<sub>4</sub>-hν indicated no catalytic activity.

In general, the polymer yields in this polymerization were very low as compared to those of other disubstituted acetylenes. These low polymer yield seems to be caused by the high steric hindrance of bulky phenyl and trimethylsilyl groups of PTSA.

#### Polymer Structure

Fig. 7 shows the <sup>1</sup>H-NMR spectrum of poly (1-phenyl-2-trimethylsilylacetylene) [PPTSA]. It shows the phenyl protons and the vinyl protons attributable to the partial desilylation at 6.0~7.6 ppm. And it also showed the broad single peak of trimethylsilyl protons at -0.8~0.5 ppm. From the <sup>1</sup>H-NMR integration, it was found that the resulting PPTSAs are partially desilylated. The extent of

**Table 3.** Polymerization of 1-Phenyl-2-Trimethylsilylacetylene by MoCl<sub>5</sub>-Based Catalysts<sup>a</sup>

Exp. No.	Catalyst System (mole ratio)	M/C <sup>b</sup> (mole ratio)	P.Y. <sup>c</sup> (%)
1	MoCl <sub>5</sub>	50	5
2	MoCl <sub>5</sub>	100	3
3	MoCl <sub>5</sub>	200	trace
4	MoCl <sub>5</sub> -Me <sub>4</sub> Sn(1 : 1)	50	7
5	MoCl <sub>5</sub> -Me <sub>4</sub> Sn(1 : 2)	50	8
6	MoCl <sub>5</sub> -n-Bu <sub>4</sub> Sn(1 : 1)	50	13
7	MoCl <sub>5</sub> -Ph <sub>4</sub> Sn(1 : 1)	50	14
8	MoCl <sub>5</sub> -Et <sub>3</sub> Al(1 : 2)	50	trace
9	MoCl <sub>5</sub> -(i-Bu) <sub>3</sub> Al(1 : 2)	50	trace
10	MoCl <sub>5</sub> -Me <sub>3</sub> Al(1 : 2)	50	trace
11	MoCl <sub>5</sub> -Et <sub>2</sub> AlCl(1 : 2)	50	trace

<sup>a</sup>Polymerization was carried out for 24 h in chlorobenzene. Initial monomer concentration ([M]<sub>0</sub>) was 2M.<sup>b</sup>Mole ratio of monomer to catalyst.<sup>c</sup>Methanol-insoluble polymer.**Table 4.** Polymerization of 1-Phenyl-2-Trimethylsilylacetylene by Other Catalysts<sup>a</sup>

Exp. No.	Catalyst System	[M] <sub>0</sub>	Solvent	P.Y. <sup>b</sup>
1	TaCl <sub>5</sub>	1	Chlorobenzene	10
2	TaCl <sub>5</sub>	1	Toluene	9
3	NbCl <sub>5</sub>	1	Chlorobenzene	13
4	NbCl <sub>5</sub>	1	Toluene	18
5	NbBr <sub>5</sub>	1	Chlorobenzene	5
6	W(CO) <sub>6</sub> -h ν <sup>c</sup>	0.5	CCl <sub>4</sub>	7
7	Mo(CO) <sub>6</sub> -h ν <sup>c</sup>	0.5	CCl <sub>4</sub>	trace
8	Cr(CO) <sub>6</sub> -h ν <sup>c</sup>	0.5	CCl <sub>4</sub>	trace

<sup>a</sup>Polymerization was carried out at 20°C for 24 h.<sup>b</sup>Methanol-insoluble polymer.<sup>c</sup>The catalyst solutions were irradiated (wavelength 350nm) at 30°C for 1 h. Polymerization was carried out at 60°C.

desilylation was dependent on the polymerization catalyst and condition.

Fig. 8 shows the <sup>13</sup>C-NMR spectrum of PPTSA. The chemical shifts of the carbon on the phenyl substituent were 127 and 132 ppm, whereas those of the carbons on the conjugated double bond were 141 and 147ppm.

Fig. 9 shows the IR spectrum of PPTSA. The aromatic=C-H stretching band was observed at

3070cm<sup>-1</sup> and a new absorption band at 1530~1570 cm<sup>-1</sup> was found to be assigned to the conjugated double bonds of polymer backbone. The band at 840cm<sup>-1</sup> is due to the Si-C stretching.

Fig. 10 shows the UV-visible spectra of PTSA and PPTSA. The UV-visible spectrum of PPTSA gives a characteristic peak of conjugated polymer, broad and weak π→π\* absorption at long wavelength.

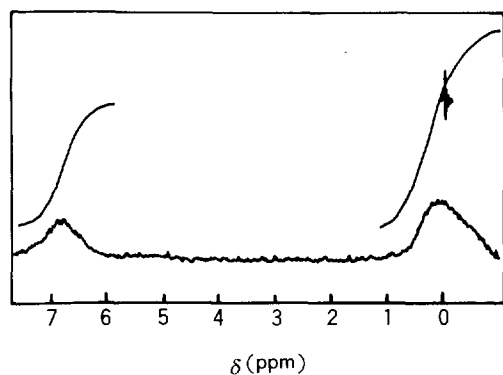


Fig. 7.  $^1\text{H}$ -NMR spectrum of poly(1-phenyl-2-trimethylsilylacetylene).

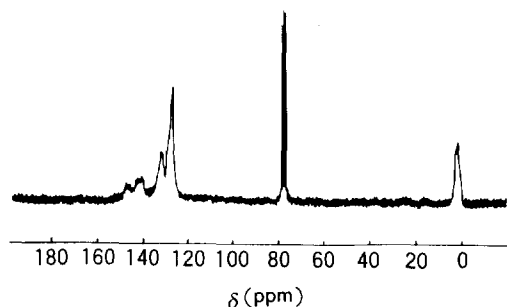


Fig. 8.  $^{13}\text{C}$ -NMR spectrum of poly(1-phenyl-2-trimethylsilylacetylene) (Solvent :  $\text{CDCl}_3$ ).

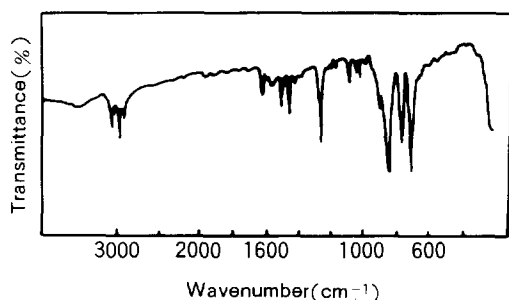


Fig. 9. IR spectrum of poly(1-phenyl-2-trimethylsilylacetylene).

From these spectral analyses, it can be concluded that the present polymer has a mostly linear conjugated polyene structure carrying some desilylated units.

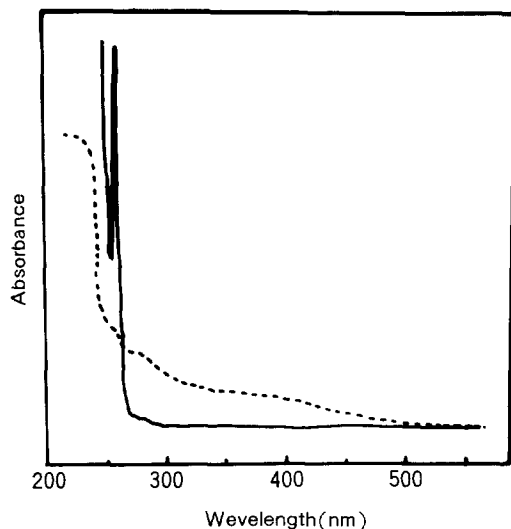


Fig. 10. UV-visible spectra of 1-phenyl-2-trimethylsilylacetylene (—) and poly(1-phenyl-2-trimethylsilylacetylene)(-----).

### Physical Properties

The number-average molecular weights (Table 5) of PPTSA were ranged from 7000 to 27100 depending upon the catalysts used. Fig. 11 shows a typical example of GPC chromatogram of PPTSA.

The TGA thermogram (Fig. 12) of PPTSA showed that it retained 95% of its original weight at 332°C, 80% at 375°C, and 30% at 600°C. Fig. 13 shows the DSC thermogram of PPTSA. The peak at 260°C might be related with the isomerization of conjugated backbone. The peak at about 350°C may be attributed to the decomposition of the polymer and to the formation of a crosslinked solid due to double bonds in the polymer backbone.

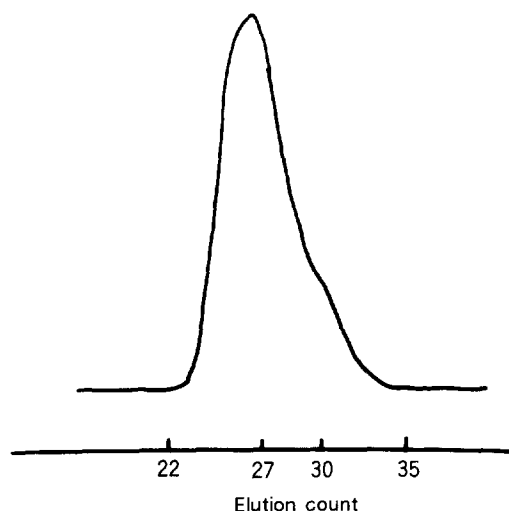
X-ray diffractogram (Fig. 14) of PPTSA showed a featureless broad peak. The ratios of half-height width to diffraction angle ( $\Delta 2\theta/2\theta$ ) are all larger than 0.20. The value for amorphous polyethylene is similar to these values, while those of crystalline polyethylene and cis-polyacetylene are much smaller. Such an amorphous character of PPTSA should be resulted from the presence of bulky substituents and/or the non-selective geometric

**Table 5.** Number-Average Molecular Weights of Poly(1-Phenyl-2-Trimethylsilylacetylene)s<sup>a</sup>

Sample No. <sup>b</sup> (c-d)	Catalyst System	$\bar{M}_n$
1-1	WCl <sub>6</sub>	24700
1-4	WCl <sub>6</sub> -Me <sub>4</sub> Sn(1 : 1)	27100
2-4	MoCl <sub>5</sub> -Me <sub>4</sub> Sn(1 : 1)	12000
4-1	TaCl <sub>5</sub>	7200
4-4	NbCl <sub>5</sub>	7000

<sup>a</sup>Number-average molecular weights were determined by GPC in tetrahydrofuran using a calibration curve of polystyrene.

<sup>b</sup>c= Table number, d= Exp. No.

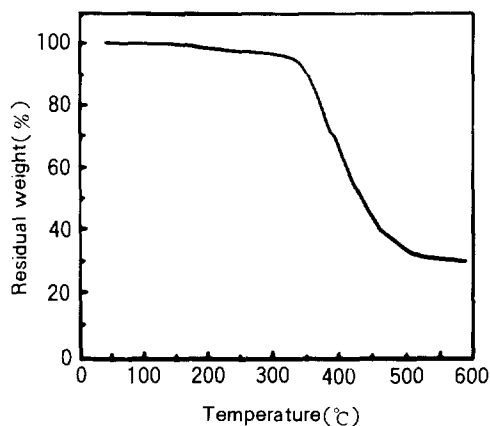
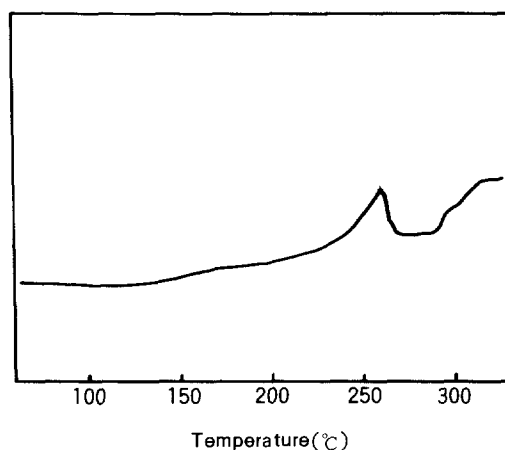
**Fig. 11.** GPC curve of poly(1-phenyl-2-trimethylsilylacetylene).

structure of the main chain.

A solubility test (Table 6) of PPTSA was performed for powdery sample in excess solvents. PPTSA is soluble in aromatic and halogenated hydrocarbons such as benzene, chloroform, CCl<sub>4</sub>, etc., and partially soluble in DMF, methyl ethyl ketone, etc., but insoluble in methanol, formic acid, hexanes, etc.

#### Desilylation Reaction

C-bonded silyl groups are widely utilized in syn-

**Fig. 12.** TGA thermogram of poly(1-phenyl-2-trimethylsilylacetylene).**Fig. 13.** DSC thermogram of poly(1-phenyl-2-trimethylsilylacetylene).

thetic organic chemistry due to their ability to stabilize charge attachment to the silicon, to undergo ipso replacement reactions, and to serve as protecting groups for acetylenes.<sup>25</sup> In recent years, the desilylation reaction of poly(trimethylsilylacetylene), monosubstituted polyacetylene containing trimethylsilyl group, has been carried out with *n*-Bu<sub>4</sub>N<sup>+</sup>F<sup>-26</sup> and HCl gas<sup>27</sup> to obtain polyacetylene. However, this reaction was not proceeded quantitatively under the various reaction conditions to yield the copolymer of trimethylsilylacetylene and



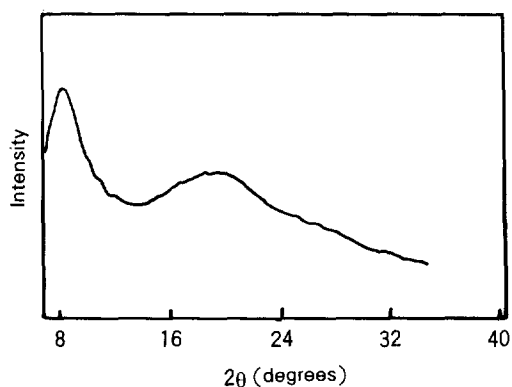


Fig. 14. X-ray diffractogram of poly(1-phenyl-2-trimethylsilylacetylene).

Table 6. Solubility Behaviors of Poly(1-phenyl-2-trimethylsilylacetylene)<sup>a</sup>

Soluble	Chloroform, Chlorobenzene, Benzene, CS <sub>2</sub> , Xylene, CCl <sub>4</sub> , THF, p-Dioxane
Partially Soluble	DMF, Methyl ethyl ketone, Triethyl amine, Methyl isobutyl ketone
Insoluble	Methanol, Ethers, Formic acid, n-Pentane, Hexanes

<sup>a</sup>The sample prepared by WCl<sub>6</sub>-Me<sub>4</sub>Sn(1 : 1) at 80°C for 24 h in chlorobenzene.

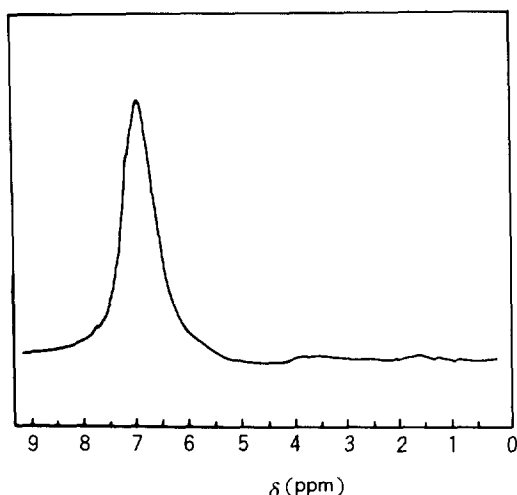


Fig. 15. <sup>1</sup>H-NMR spectrum of desilylated poly(1-phenyl-2-trimethylsilylacetylene).

acetylene. This was attributed to the insolubility of the product even at moderate conversion.

We tried the desilylation reaction of PPTSA by *n*-Bu<sub>4</sub>N<sup>+</sup>F<sup>-</sup>, HCl, and HF. *n*-Bu<sub>4</sub>N<sup>+</sup>F<sup>-</sup> desilylated PPTSA completely to give poly(phenylacetylene). However, HCl and HF did not desilylate PPTSA. The NMR(<sup>1</sup>H- and <sup>13</sup>C-) and IR spectra of poly(phenylacetylene) prepared by desilylation of PPTSA by *n*-Bu<sub>4</sub>N<sup>+</sup>F<sup>-</sup> are shown in Figs 15~17. These spectra were the same as those of poly(phenylacetylene) prepared by the polymerization of phenylacetylene by WCl<sub>6</sub>.<sup>28</sup> This complete desilyla-

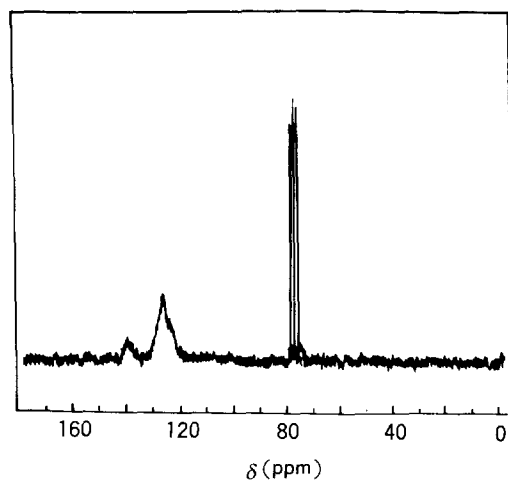


Fig. 16. <sup>13</sup>C-NMR spectrum of desilylated poly(1-phenyl-2-trimethylsilylacetylene) (Solvent : CDCl<sub>3</sub>).

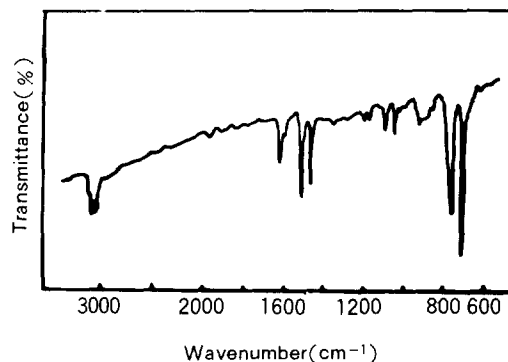


Fig. 17. IR spectrum of desilylated poly(1-phenyl-2-trimethylsilylacetylene).

tion can be attributed to the good solubility of the resulting poly(phenylacetylene).

## CONCLUSIONS

Silicon containing disubstituted polyacetylene, PPTSA, was synthesized by various transition metal catalysts. The highest polymer yield(33%) was obtained when the mole ratio of PTSA to  $WCl_6$  and  $Me_4Sn$  to  $WCl_6$  were 50 and 1, respectively. From spectral analyses, it was found that the resulting PPTSA is partially desilylated one. X-ray diffraction analysis indicated that the PPTSA has no crystallinity. PPTSA was soluble in aromatic and halogenated hydrocarbons such as chloroform, benzene,  $CCl_4$ , etc. and completely desilylated by  $n-Bu_4N^+F^-$  to give poly(phenylacetylene).

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