

## 전이금속촉매에 의한 프로파길 벤젠술폰에이트의 중합

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(1991년 10월 30일 접수)

### Polymerization of Propargyl Benzenesulfonate by Transition Metal Catalysts

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(Received October 30, 1991)

**요 약 :** 여러가지 전이금속촉매를 사용하여 프로파길 벤젠술폰에이트(PBS)를 중합시켜 술폰에이트 기능을 갖는 새로운 공액구조 고분자를 합성하였다. Mo-계 촉매가 W-계 촉매보다 본 중합에 더 효과적이었으며 특히 MoCl<sub>5</sub>-유기알루미늄 촉매가 매우 효과적인 것으로 밝혀졌다. W 및 Mo 에톡사이드-EtAlCl<sub>2</sub> 역시 PBS를 효과적으로 중합하였다. PdCl<sub>2</sub>와 PtCl<sub>2</sub>를 사용하여 PBS를 중합시킨 결과 높은 수율의 고분자를 합성할 수 있었다. 생성된 폴리(PBS)들은 사용한 촉매와 중합조건에 관계없이 유기용매에 용해하지 않았으며 검은색의 분말형이었다. 폴리(PBS)들의 열특성에 관해서도 연구하였다.

**Abstract :** A new conjugated polymer containing sulfonate functional group was synthesized by the polymerization of propargyl benzenesulfonate(PBS) with various transition metal catalysts. Mo-based catalysts were more effective than W-based catalysts. Especially MoCl<sub>5</sub>-organoaluminum catalysts were very effective. W and Mo ethoxide-EtAlCl<sub>2</sub> catalysts were also found to be very active for this polymerization. PdCl<sub>2</sub> and PtCl<sub>2</sub> also polymerized PBS to produce a high yield of polymer. The resulting poly(PBS) were insoluble in organic solvents regardless of catalysts used. This polymer was dark colored powder. Thermal properties of poly(PBS) were also studied.

#### INTRODUCTION

The polymerization of propargyl derivatives, some monosubstituted acetylenes, have been carried out by various initiating systems : <sup>1-3</sup> The

polymerization of propargyl halide (halide = Br, Cl) was attempted using catalysts such as PdCl<sub>2</sub>, <sup>4</sup>  $\gamma$ -ray, <sup>5-6</sup> NiI<sub>2</sub>(Ph<sub>3</sub>P)<sub>2</sub>, <sup>7</sup> W(CO)<sub>6</sub>-CCl<sub>4</sub>-hv, <sup>8,9</sup> MoCl<sub>5</sub>, <sup>10,11</sup> MoCl<sub>5</sub>-polymer, <sup>12</sup> etc. However the resulting polymers prepared by these catalysts were insoluble in

any organic solvents.

Recently the soluble poly(propargyl bromide) and poly(propargyl chloride) were prepared by Mo- and W-based catalysts in many research groups.<sup>13~15</sup> Oxygen-containing propargyl derivatives such as propargyl alcohol and propargyl ethers were also polymerized by a variety of catalysts including PdCl<sub>2</sub>,<sup>4</sup> MoCl<sub>5</sub>,<sup>10</sup> Plasma,<sup>16</sup> [Ni(NCS) (C≡CCH<sub>2</sub>OH)(PPh<sub>3</sub>)<sub>2</sub>],<sup>7</sup> C<sub>6</sub>H<sub>5</sub>C≡W(CO)<sub>4</sub>Br,<sup>17</sup> WCl<sub>6</sub>-Et<sub>2</sub>AlCl,<sup>18</sup> MoCl<sub>5</sub>-EtAlCl<sub>2</sub>,<sup>19</sup> MoCl<sub>5</sub>-n-Bu<sub>4</sub>Sn.<sup>20</sup> To date, there is a few studies for the synthesis of sulfur-containing polyacetylene derivatives. We reported the polymerization of acetylene derivatives carrying the pendent thienyl group<sup>22,23</sup> and the cyclopolymerization of dipropargyl sulfide.<sup>24</sup> 1-(n-Alkylthio)-1-propynes, sulfur-containing analogues of 2-alkynes were polymerized and characterized.<sup>25</sup> The resulting polymers were colorless, soluble, film formable ones having high molecular weights (MW = 1 × 10<sup>5</sup> - 2 × 10<sup>5</sup>).

However there have been no reports on the polymerization of propargyl benzenesulfonate (PBS) having two hetero atoms, sulfur and oxygen. The present paper deals with the polymerization behaviors of PBS by various transition metal catalysts and the characterization of the resulting poly(propargyl benzenesulfonate)[poly(PBS)].

## EXPERIMENTAL

### Materials

PBS(Aldrich Chemicals, 97%, bp 140-142°C/2 mmHg) was dried with magnesium sulfate and fractionally distilled under reduced pressure. Tungsten(VI) and molybdenum(V) chlorides (Aldrich Chemicals, resublimed, 99+ %) and tungsten(VI) and molybdenum(V) ethoxides (High purity chemicals) were used as received. Palladium(II) chloride(Aldrich chemicals, 99.995%) and Platinum(II) chloride(Strem) were used as received. Organoaluminum compounds [Et<sub>3</sub>Al, Et<sub>2</sub>AlCl, Et<sub>2</sub>AlCl<sub>2</sub>, Aldrich Chemicals, 25 wt% (1.8M) solution in toluene] were used without further purification. Tetraphenyltin (Ph<sub>4</sub>Sn, Aldrich Chemicals,

97%) was purified by recrystallizing twice from carbon tetrachloride. All polymerization solvents were analytical grade materials. They were dried with appropriate drying agent and fractionally distilled before use.

### Instruments

Infrared spectra were taken on a Bio-Rad Digilab FTS-60 spectrometer using potassium bromide pellets. Thermogravimetric analysis(TGA) was performed under nitrogen atmosphere at a heating rate of 10°C/min with Dupont 951 Thermogravimetric Analyzer. Thermal transitions were measured with Dupont 910 differential scanning calorimeter under nitrogen atmosphere at a heating rate of 10°C/min.

### Polymerization Procedures

The examples of polymerization are described below. After a given period of polymerization, the polymerization was stopped by adding a small amount of methanol. Then, the polymerization mixture was diluted with 10 ml of chloroform. The resulting polymer was purified by pouring in a large excess of methanol. The polymer was filtered from the solution and dried to a constant weight under vacuum at 60°C for 24 hr. The polymer yield was calculated by gravimetry.

#### Polymerization of PBS by MoCl<sub>5</sub>

A solution of MoCl<sub>5</sub>(1.02 ml 0.05 M chlorobenzene solution, 0.051 mmol) and chlorobenzene (1.13 ml, [M]<sub>0</sub> = 1) is prepared. To this solution is added PBS(0.5g, 2.55mmol) at room temperature and the polymerization was carried out at 60°C for 24hr. After 1 hr, brown colored polymers was precipitated into the bottom of polymerization ampule. Polymerization did not proceed further after 2hr to obtain 5% of polymer yield.

#### Polymerization of PBS by Mo(OEt)<sub>3</sub>-EtAlCl<sub>2</sub>

A catalyst solution is prepared by mixing Mo(OEt)<sub>3</sub> (0.255ml 0.2M chlorobenzene solution, 0.051mmol), EtAlCl<sub>2</sub> (0.51ml 0.2M chlorobenzene solution, 0.102mmol), and chlorobenzene(1.385ml, [M]<sub>0</sub> = 1) and aged by keeping at 30°C for 15 min. To this solution is added PBS(0.5g, 2.55mmol). Polymerization was carried out at 60°C for 24hr. As

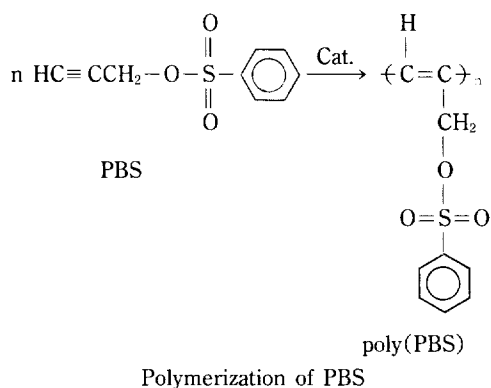
the polymerization time increased, the polymerization solution changed into gel and finally solid-like state. After a given period of polymerization, the black-colored polymer was formed in the polymerization ampule. Polymer yield was 83%.

#### Polymerization of PBS by PdCl<sub>2</sub>

PdCl<sub>2</sub> (9.04mg, 0.051mmol) was dissolved in DMF(4.69ml, [M]<sub>0</sub>=0.5) at 90°C. To this catalyst solution, PBS(0.5g, 2.55mmol) was added at 90°C. The polymerization was proceeded more slowly than those of W- and Mo-based catalysts. And the polymerization solution was black after a given period of polymerization (24hr). An exothermic phenomenon was observed when a small amount of methanol is added. Polymer yield was 79%.

## RESULTS AND DISCUSSION

The polymerization of PBS, propargyl derivative containing benzoate functional group, was carried out with a variety of transition metal-based catalysts.



Mo-based catalysts was firstly tested for this polymerization because MoCl<sub>5</sub> was found to be very active for some acetylene derivatives having oxygen atom<sup>20,24</sup> and polar-functional group.<sup>14,26~28</sup> Table 1 shows the results for the polymerization of PBS by Mo-based catalysts. MoCl<sub>5</sub> alone gave only a low yield of polymer. Ph<sub>4</sub>Sn, which was very effective cocatalyst for the polymerization of phenylacetylene<sup>26</sup> and 2-ethynylthiophene<sup>22</sup> by MoCl<sub>5</sub> or WCl<sub>6</sub>, did not show any cocatalytic effect.

**Table 1.** Polymerization of Propargyl Benzenesulfonate(PBS) by Mo-Based Catalysts<sup>a</sup>

Exp. No	Catalyst System <sup>b</sup> (mole ratio)	M/C <sup>c</sup>	[M] <sub>0</sub> <sup>d</sup>	Temp. (°C)	P.Y. <sup>e</sup> (%)
1	MoCl <sub>5</sub>	50	1	60	5
2	MoCl <sub>5</sub> -Ph <sub>4</sub> Sn(1 : 1)	50	1	60	2
3	MoCl <sub>5</sub> -Et <sub>3</sub> Al(1 : 2)	50	1	60	67
4	MoCl <sub>5</sub> -Et <sub>2</sub> AlCl(1 : 2)	50	1	60	71
5	MoCl <sub>5</sub> -EtAlCl <sub>2</sub> (1 : 2)	50	1	60	76
6	MoCl <sub>5</sub> -EtAlCl <sub>2</sub> (1 : 2)	100	1	60	43
7	MoCl <sub>5</sub> -EtAlCl <sub>2</sub> (1 : 2)	50	2	60	80
8	MoCl <sub>5</sub> -EtAlCl <sub>2</sub> (1 : 2)	50	1	30	11
9	MoCl <sub>5</sub> -EtAlCl <sub>2</sub> (1 : 2)	50	1	90	85
10	Mo(OEt) <sub>5</sub>	50	1	60	5
11	Mo(OEt) <sub>5</sub> -EtAlCl <sub>2</sub> (1 : 2)	50	1	60	83

<sup>a</sup> Polymerization was carried out for 24 hr in chlorobenzene.

<sup>b</sup> Mixture of catalyst and cocatalyst was aged at 30°C for 15 min.

<sup>c</sup> Monomer to catalyst mole ratio.

<sup>d</sup> Initial monomer concentration.

<sup>e</sup> Polymer yield.

However organoaluminum compounds, which have been used as the cocatalyst for the metathesis reaction of olefins<sup>30,31</sup> and the metathesis polymerization of cycloolefins<sup>32~33</sup> by W- and Mo- chlorides, showed a high cocatalytic activity for this polymerization. Three organoaluminum compounds, Et<sub>3</sub>Al, Et<sub>2</sub>AlCl, and EtAlCl<sub>2</sub>, showed a similar cocatalytic activity. When monomer to catalyst mole ratio is increased from 50 to 100, the polymer yield was decreased from 76% to 43%. The enhanced decrease of polymer yield by increasing monomer to catalyst mole ratio is due to the relatively low catalyst amount and/or the decrease of catalytic activity by the interaction of catalyst with the heteroatom of monomer, PBS. Molybdenum ethoxide was also used for this polymerization. Mo(OEt)<sub>5</sub> alone gave a low yield of polymer. However the polymer yield increased notably to 83% when EtAlCl<sub>2</sub> was used as a cocatalyst. This finding for the high catalytic activity of Mo(OEt)<sub>5</sub>-EtAlCl<sub>2</sub> system is very interesting phenomenon

although the polymerization mechanism has not been fully understood.

Table 2 shows the results for the polymerization of PBS by W-based catalysts. W-based catalyst systems gave mostly a low yield of polymer.  $\text{Ph}_4\text{Sn}$  and organoaluminum compounds did not show any cocatalytic activity.

This low catalytic activity of  $\text{WCl}_6$ -based catalyst, was also observed for the polymerization of similar propargyl derivatives containing oxygen<sup>11</sup> and sulfur<sup>24</sup> atoms. Only  $\text{W}(\text{OEt})_6$ - $\text{EtAlCl}_2$  system gave 45% yield of polymer although the polymerization mechanism is not understood. In the polymerization of PBS by  $\text{W}(\text{OEt})_6$ - $\text{EtAlCl}_2$ , the polymer yield decreased notably as the monomer to catalyst mole ratio (M/C) increased.

Table 3 shows the results for the polymerization of PBS by  $\text{PdCl}_2$  and  $\text{PtCl}_2$ .  $\text{PdCl}_2$ , which was used for the polymerization of propargyl derivatives such as propargyl alcohol, methyl propargyl ether, dimethyl propargyl amine etc.,<sup>4</sup> was also very effective for this polymerization. The polar solvents

**Table 2.** Polymerization of Propargyl Benzenesulfonate(PBS) by W-Based Catalysts<sup>a</sup>

Exp. No.	Catalyst System <sup>b</sup> (mole ratio)	M/C <sup>c</sup>	$[\text{M}]_0^d$	P.Y. <sup>e</sup> (%)
1	$\text{WCl}_6$	50	1	0
2	$\text{WCl}_6$ - $\text{Ph}_4\text{Sn}$ (1 : 1)	50	1	2
3	$\text{WCl}_6$ - $\text{Et}_3\text{Al}$ (1 : 2)	50	1	5
4	$\text{WCl}_6$ - $\text{Et}_2\text{AlCl}$ (1 : 2)	50	1	3
5	$\text{WCl}_6$ - $\text{EtAlCl}_2$ (1 : 2)	50	1	7
6	$\text{W}(\text{OEt})_6$	50	1	0
7	$\text{W}(\text{OEt})_6$ - $\text{EtAlCl}_2$ (1 : 2)	50	1	45
8	$\text{W}(\text{OEt})_6$ - $\text{EtAlCl}_2$ (1 : 2)	100	1	20
9	$\text{W}(\text{OEt})_6$ - $\text{EtAlCl}_2$ (1 : 2)	250	1	5
10	$\text{W}(\text{OEt})_6$ - $\text{EtAlCl}_2$ (1 : 2)	50	0.5	12

<sup>a</sup> Polymerization was carried out at 60°C for 24hr in chlorobenzene.

<sup>b</sup> Mixture of catalyst and cocatalyst was aged at 30°C for 15 min.

<sup>c</sup> Monomer to catalyst mole ratio.

<sup>d</sup> Initial monomer concentration.

<sup>e</sup> Polymer yield.

were used because  $\text{PdCl}_2$  and  $\text{PtCl}_2$  are mostly insoluble in some aromatic solvents and halogenated hydrocarbon solvents such as chlorobenzene, toluene, and  $\text{CCl}_4$  etc., and the catalyst solutions are inhomogeneous. The relatively high polymer yield was obtained in DMF, DMSO, and pyridine solvents.  $\text{PtCl}_2$  also polymerized PBS to give poly(PBS), but the yield was lower than those of  $\text{PdCl}_2$ .

The resulting poly(PBS)s were mostly black colored powder. The poly(PBS)s, regardless of polymerization catalyst, were insoluble in organic solvents. The similar solubility behaviors were observed for the polymers from propargyl derivatives such as propargyl alcohol,<sup>14</sup> propargyl ethers,<sup>14</sup> and dipropargyl ether.<sup>18</sup> This insolubility seemed to be due to the cross-linking of active allyl protons of polymer by catalyst moiety.

Fig. 1 shows the FT-IR spectra of PBS and poly(PBS). Peaks at 3283 and 2132 $\text{cm}^{-1}$  of IR spectrum of PBS which are corresponded to the acetylenic  $\equiv \text{C-H}$  and  $\text{C} \equiv \text{C}$  stretching, respectively, disappeared as the result of polymerization. Instead, the carbon-carbon double bond (in the polymer backbone) stretching frequency along with the characteristic frequencies of sulfonate and phenyl substituent was observed at 1550~1730 $\text{cm}^{-1}$ .<sup>34</sup>

**Table 3.** Polymerization of Propargyl Benzenesulfonate(PBS) by  $\text{PdCl}_2$  and  $\text{PtCl}_2$ <sup>a</sup>

Exp. No.	Catalyst System	M/C <sup>b</sup>	Solvent	P.Y. <sup>c</sup>
1	$\text{PdCl}_2$	30	DMF	85
2	$\text{PdCl}_2$	50	DMF	79
3	$\text{PdCl}_2$	50	DMSO	75
4	$\text{PdCl}_2$	50	Pyridine	77
5	$\text{PdCl}_2$	50	Nitrobenzene	46
6	$\text{PdCl}_2$	50	Formic acid	60
7	$\text{PdCl}_2$	50	Ethanol	42
8	$\text{PtCl}_2$	50	DMF	50
9	$\text{PtCl}_2$	50	DMSO	54

<sup>a</sup> Polymerization was carried out at 90°C for 24hr. Initial monomer concentration ( $[\text{M}]_0$ ) was 0.5 M.

<sup>b</sup> Monomer to catalyst mole ratio.

<sup>c</sup> Polymer yield.

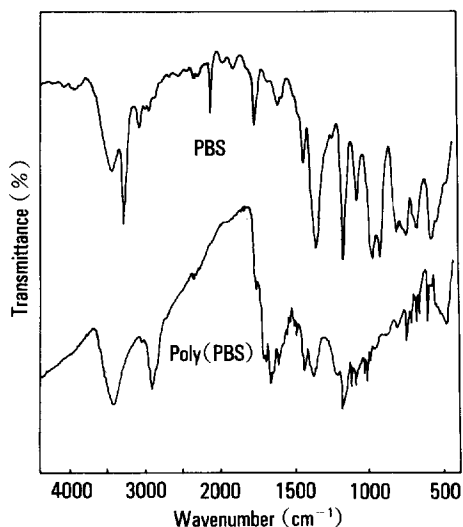


Fig. 1. FT-IR spectra of propargyl benzenesulfonate (PBS) and poly(PBS).

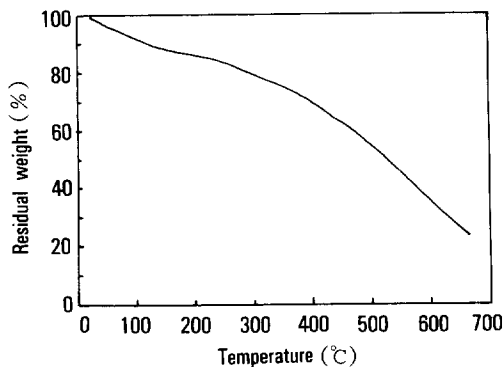


Fig. 2. TGA thermogram of poly(PBS).

The TGA thermogram (Fig. 2) of poly(PBS) prepared by  $\text{MoCl}_5\text{-EtAlCl}_2$  shows a little weight loss at relatively low temperature. It can be seen that poly(PBS) retained 90% of its original weight at 125°C, 80% at 285°C, and 60% at 458°C. Similar behaviors, a weight loss at low temperatures, were also reported for poly(dipropargyl ether)<sup>18</sup> and poly(2-ethynylpyridine).<sup>35</sup> The weight loss at low temperature seems to be due to the moisture, solvents, and catalyst residues although it is not fully characterized. The DSC thermogram (Fig. 3) of poly(PBS) prepared by  $\text{MoCl}_5\text{-EtAlCl}_2$  shows a broad endo-

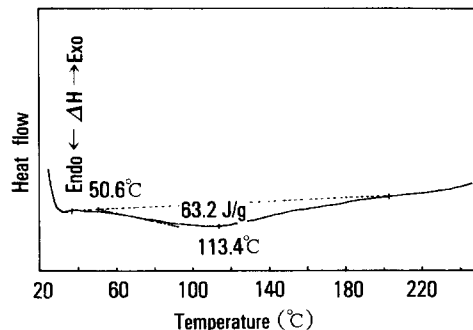


Fig. 3. DSC thermogram of poly(PBS).

thermic peak (maximum peak temperature : 113.4°C).

In conclusion, a new conjugated polymer, poly (PBS), was synthesized and characterized. Mo-based catalysts were more effective than that of W-based catalysts. Mo and W ethoxide- $\text{EtAlCl}_2$  catalyst system was also found to be very effective. Classical  $\text{PdCl}_2$  and  $\text{PtCl}_2$  also polymerized PBS to give a good yield of polymer. The resulting poly (PBS)s were black colored powder. The poly (PBS)s were insoluble in any organic solvents, which seemed to be due to the cross-linking of resulting polymer containing active allyl protons.

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