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## A HIGHLY CONJUGATED POLYMER FROM TETRAPROPARGYLAMMONIUM BROMIDE

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### ABSTRACT

A highly conjugated polymer was synthesized by the polymerization of multiacetylenic compound, tetrapropargylammonium bromide (TPAB), with various transition metal catalysts in high yields. PdCl<sub>2</sub>, PtCl<sub>2</sub>, RuCl<sub>3</sub>, MoCl<sub>5</sub>-EtAlCl<sub>2</sub>, and WCl<sub>6</sub>-EtAlCl<sub>2</sub> were found to be effective for the polymerization of TPAB. Various possible polymer structures were suggested for poly(TPAB) via different cyclopolymerization pathways of tetrapropargyl functional groups. The resulting polymers were insoluble in organic solvents, and black or brown powder.

### INTRODUCTION

The conjugated polymers are known to show unique properties such as electrical conductivity,<sup>1-3</sup> gas and liquid mixture separation,<sup>4-6</sup> side chain liquid crystal,<sup>7,8</sup> and electron-beam resist materials.<sup>9,10</sup> A number of polyacetylenes with substituent have been synthesized and characterized.<sup>11-13</sup> However the conjugated ionic polymers were scarce and

restricted to some cases as follows: the solid polymerization of propiolic salts by  $\gamma$ -irradiation,<sup>14</sup> water-soluble polyene polymers by quaternarization of poly(6-bromo-1-hexyne),<sup>15</sup> the synthesis of mono- and di-substituted ionic polyacetylene by the activation of the acetylene bond in ethynylpyridine by the introduction of a strong electron withdrawing substituents in conjugation to it.<sup>16-18</sup>

In a series of our recent works, various ionic propargyl monomers such as propargyltriphenylphosphonium bromide,<sup>19</sup> dipropargyldihexyl ammonium salts (counter anion: Br<sup>-</sup>, CH<sub>3</sub>--SO<sub>3</sub><sup>-</sup>, BPh<sub>4</sub><sup>-</sup>),<sup>20,21</sup> and tripropargylammonium bromide<sup>22</sup> were synthesized and effectively polymerized.

The present paper reports on the synthesis and characterization of a highly conjugated polyacetylene derivatives by the simple polymerization of tetrapropargylammonium bromide (TPAB) having four polymerizable acetylenic functional group per monomeric unit.

#### EXPERIMENTAL

Tripropargylamine (Aldrich Chemicals., 98%) and propargyl bromide (Aldrich Chemicals., 80 wt% solution in toluene) were used as received. TPAB was prepared by the reaction of tripropargylamine and propargyl bromide in acetonitrile at room temperature (yield: 85%). The resulting TPAB was purified by recrystallization from methanol. <sup>1</sup>H-NMR (DMSO-d<sub>6</sub>,  $\delta$ , ppm) : 4.19, 4.53 ; <sup>13</sup>C-NMR (DMSO-d<sub>6</sub>,  $\delta$ , ppm) : 50.1, 70.6, 84.7 ; IR (wavenumbers, cm<sup>-1</sup>) : 3162 ( $\equiv$ C-H stretching), 2124 (C=C stretching).

PdCl<sub>2</sub> (Aldrich Chemicals, 99.995%), PtCl<sub>2</sub> (Aldrich Chemicals, 98%), and RuCl<sub>3</sub> (Aldrich Chemicals) were used as received. MoCl<sub>5</sub> and WCl<sub>6</sub> (Aldrich Chemicals., resublimed, 99+%) and EtAlCl<sub>2</sub> (Aldrich Chemicals, 1.8 M solution in toluene) was used as received. All polymerization solvents were analytical grade materials. They were dried with appropriate drying agents and fractionally distilled. A polymerization ampule equipped with rubber septum was flushed with dry nitrogen. The polymerization was carried out as described earlier<sup>22</sup>. The resulting polymer was precipitated into excess ethyl ether.

Solid state <sup>13</sup>C-NMR spectra of polymer were recorded on a Bruker AM-300 spectrometer at magic spinning angle. Infrared spectra were obtained with

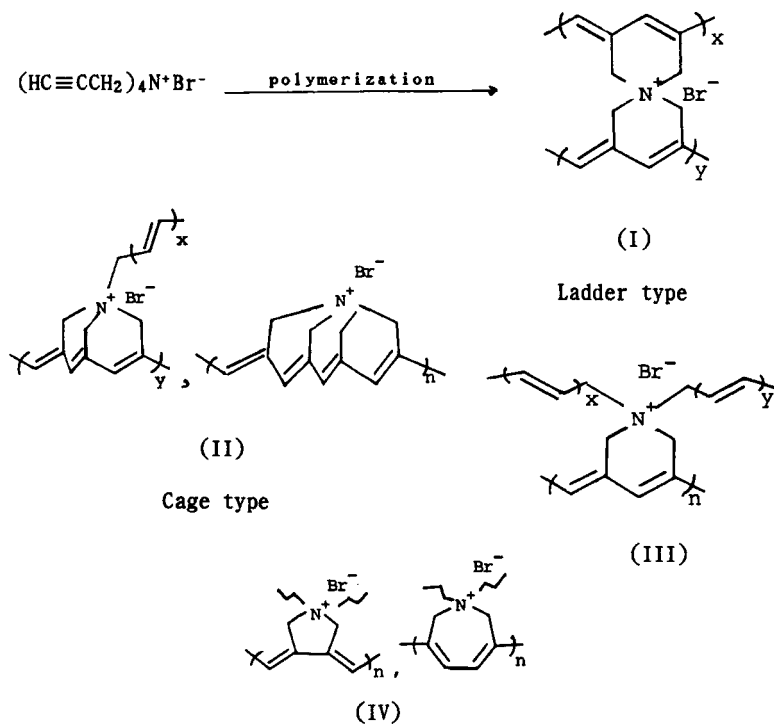
a Bio-Rad Digilab FTS-60 spectrometer using potassium bromide pellets. Thermogravimetric analyses (TGA) were performed under nitrogen atmosphere at a heating rate of 10°C/min upto 700°C with a DuPont 1090 Analyzer.

## RESULTS AND DISCUSSION

TPAB was polymerized by various transition metal catalysts to give poly(TPAB) having four conjugated double bond per monomeric unit (Scheme I).

The results for the polymerization of TPAB by various transition metal catalysts are listed in Table 1. PdCl<sub>2</sub>, PtCl<sub>2</sub>, and RuCl<sub>3</sub> were mostly found to be effective catalysts for the present polymerization of multipropargylammonium salts. Four polymerization solvents were tested. DMF and DMSO gave good results and pyridine exhibited a moderate yield of polymer. On the other hand, the polymerization did not proceed at formic acid. The polymerization seemed to be proceeded as somewhat heterogeneous phase. The Mo- and W-based catalysts, which have been known to be effective catalysts for the polymerization of such acetylene derivatives as 2-ethynylpyridine,<sup>23</sup> propargyl bromide,<sup>24</sup> and dipropargyl sulfoxide,<sup>25</sup> were also tested for the present polymerization of multipropargylammonium bromides. MoCl<sub>5</sub> and WCl<sub>6</sub> alone failed to polymerize TPAB. Ph<sub>4</sub>Sn did not show a cocatalytic activity at the polymerization of TPAB by MoCl<sub>5</sub>. However the polymer yields were quantitative when the organoaluminum cocatalyst, EtAlCl<sub>2</sub>, was used for the polymerization of TPAB by MoCl<sub>5</sub> and WCl<sub>6</sub>.

The resulting poly(TPAB)s were mostly insoluble in organic solvents as like with the polymer of tripropargylammonium bromide, regardless of the polymerization conditions and the catalysts used. The poly(TPAB)s obtained were brown or black powder. The insolubility of poly(TPAB)s may be originated from the chain rigidity of the conjugated polymer and/or the crosslinking of polymer chain by the catalytic moiety. In the present time, the assignment of the exact poly(TPAB) structure is very difficult. As shown in Scheme I, various polymer structures are probable because the four polymerizable acetylenic functions are presented in the monomer. And also the crosslinked products, which is caused by the activated methylene moiety, may be presented.



+ Other crosslinked product caused by the active allyl protons of methylene carbons

Scheme I. Polymerization of TPAB and Possible Structures of Poly(TPAB)

Table 1. Polymerization of TPAB by Transition Metal 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> (M)	Solvent	Polymer Yield (%)
1	PdCl <sub>2</sub>	30	0.3	DMF	64
2	PdCl <sub>2</sub>	15	0.3	DMF	90
3	PdCl <sub>2</sub>	15	0.15	DMF	51
4	PdCl <sub>2</sub>	15	0.3	DMSO	93
5	PdCl <sub>2</sub>	15	0.3	Pyridine	65
6	PdCl <sub>2</sub>	15	0.3	HCO <sub>2</sub> H	0
7	PtCl <sub>2</sub>	15	0.3	DMF	77
8	RuCl <sub>3</sub>	15	0.3	DMF	56
9	MoCl <sub>5</sub>	30	0.5	Chlorobenzene	0
10	MoCl <sub>5</sub> -Ph <sub>4</sub> Sn(1:1)	30	0.5	Chlorobenzene	0
11	MoCl <sub>5</sub> -EtAlCl <sub>2</sub> (1:2)	30	0.5	Chlorobenzene	99
12	WCl <sub>6</sub>	30	0.5	Chlorobenzene	0
13	WCl <sub>6</sub> -EtAlCl <sub>2</sub> (1:2)	30	0.5	Chlorobenzene	95

<sup>a</sup>Polymerization was carried out at 90°C for 24 hrs.

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

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

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

Fig. 1 shows the IR spectra of TPAB and poly(TPAB) in KBr pellets. The IR spectrum of poly(TPAB) showed neither the most acetylenic  $\equiv\text{C-H}$  stretching ( $3162\text{ cm}^{-1}$ ) nor the  $\text{C}\equiv\text{C}$  triple bond stretching ( $2124\text{ cm}^{-1}$ ) frequencies observed in the IR spectrum of TPAB. Instead the  $\text{C}=\text{C}$  double bond stretching frequency of polymer backbone was newly observed at about  $1634\text{ cm}^{-1}$ . However, even at the IR spectrum of polymer, small peaks (at  $3161$  and  $2124\text{ cm}^{-1}$ ), characteristics of acetylenic functional groups were also observed. This indicates that the present tetrafunctional monomers are difficult to be completely polymerized because of its molecular structure and the steric hinderance of the resulting polymers.

Fig. 2 shows the magic angle spinning, cross polarization  $^{13}\text{C-NMR}$  spectrum of poly(TPAB) prepared by PdCl<sub>2</sub>. The chemical shift at about  $134\text{ ppm}$  is

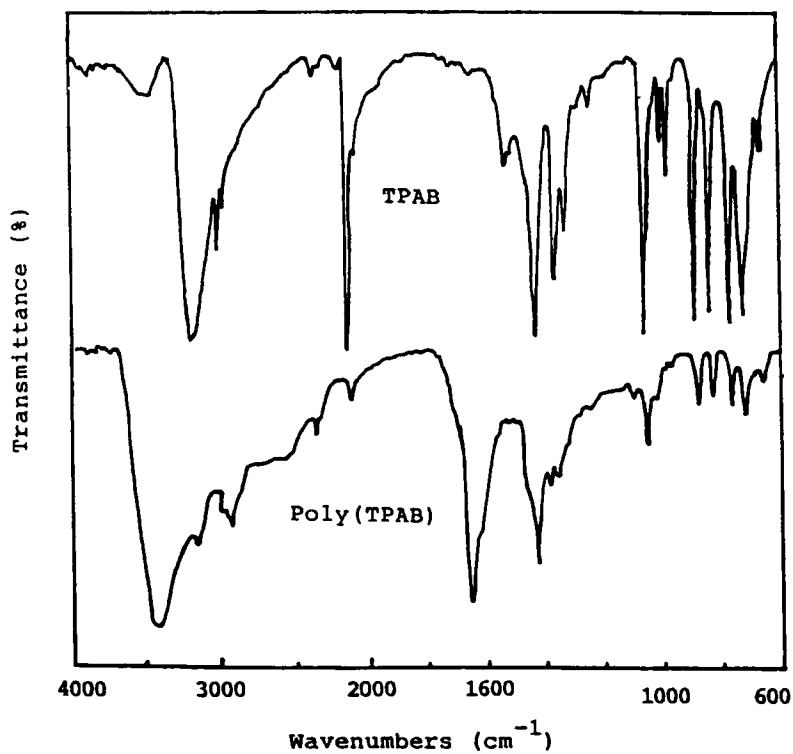


Fig. 1. FT-IR spectra of TPAB and poly(TPAB) in KBr pellet.

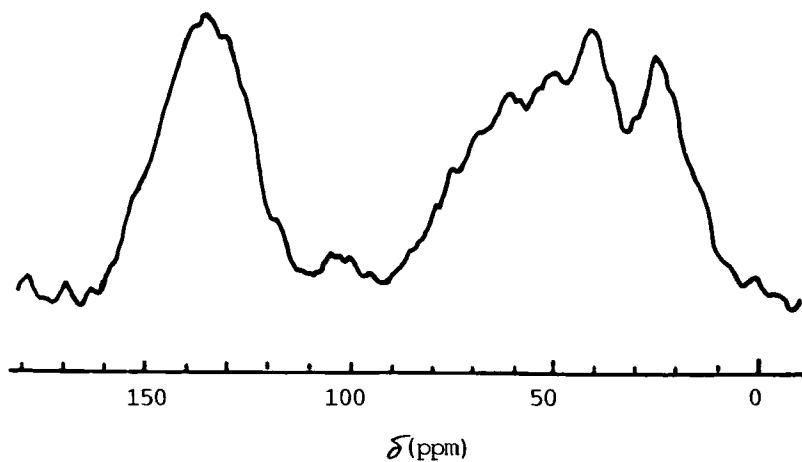


Fig. 2. <sup>13</sup>C magic angle spinning-cross polarization NMR spectra of poly (TPAB)

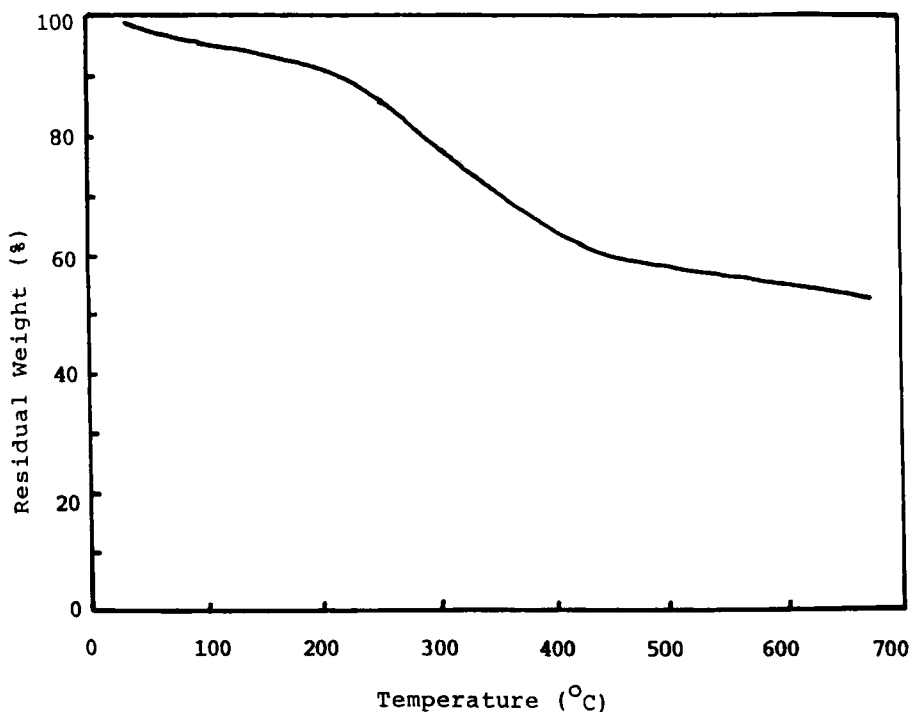


Fig. 3. TGA thermogram of poly(TPAB)

due to the carbons on the conjugated double bond of polymer backbone. And the broad methylene carbon peaks are also observed in the range range of 15 and 80 ppm.

Fig. 3 shows the TGA thermogram of poly(TPAB) prepared by  $\text{PdCl}_2$ . This polymer showed a gradual weight loss from the low temperature. This shows that the poly(TPAB) retaining 90% of its original weight at 200°C, 78% at 300°C, 64% at 400°C, and 51% at 700°C. The weight loss at low temperatures is due to the absorbed moisture and solvents although it is not fully characterized.

The color of polymers prepared by  $\text{PdCl}_2$  and  $\text{PtCl}_2$  were mostly black. On the other hand, the polymers prepared by W- and Mo-based catalysts were brown color.



## CONCLUSIONS

The synthesis and characterization of a highly conjugated polymer by the cyclopolymerization of tetraacetylenic compound, TPAB, by various transition metal catalysts were described. The polymerization was easily proceeded to give a high yield of polymer. The resulting poly(TPAB)s were insoluble in organic solvents and black or brown powder. The insolubility of the resulting polymers was judged to be due to the rigidity of the conjugated polymer chain and/or the cross-linking of polymer by the catalytic moiety. Various probable polymer structures were suggested for the highly conjugated poly(TPAB).

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