

# UV LASER INITIATED STEREOSELECTIVE HOMOGENEOUS CATALYSIS POLYMERIZATION OF PHENYLACETYLENE

ZHANG Jie (张杰), SHE Yongbo (余永柏) and FU Kejian (傅克坚)\*

(*Institute of Physics, Chinese Academy of Sciences, Beijing 100080*)

ZHOU Yihua (周以华)

(*National Center for Certified Reference Materials, Beijing 100013*)

## ABSTRACT

In this paper, the stereoselective homogeneous catalysis polymerization of phenylacetylene by using two kinds of catalysts  $W(CO)_5CH_3I$  and  $W(CO)_4I_2$  produced from UV laser photolysis of  $W(CO)_6$  in  $CH_3I$ ,  $I_2-C_6H_6$  and  $CHI_3-C_6H_6$  respectively was studied. The effects of laser energy, laser irradiation time and lifetime of catalyst on the polymerization of phenylacetylene were discussed. The photoproducts of  $W(CO)_6$  in  $CH_3I$ ,  $I_2-C_6H_6$  and  $CHI_3-C_6H_6$  were determined by IR spectra. The structures of polyphenylacetylene obtained by  $W(CO)_5CH_3I$  and  $W(CO)_4I_2$  catalysts were characterized by IR spectra and  $^1H$  NMR spectra.

## INTRODUCTION

Under the activation of UV light, metal carbonyl compounds easily lose one or several CO to give coordinatively unsaturated intermediates which are potent catalysts. The coordinatively unsaturated metal carbonyl has been used in the selectively catalytic reaction, such as the isomerization<sup>[1]</sup>, hydrogenation<sup>[2]</sup> and dehydrogenation<sup>[3]</sup> in mild conditions. Therefore, the study on the photochemistry of metal carbonyl compounds has attracted considerable attention. Recently, the metal carbonyl compounds as catalyst precursor were used for the polymerization of alkyne and cycloalkene, especially the photo-induced heterogeneous catalysis polymerization of alkynes and cycloalkenes by  $W(CO)_6-CCl_4$  system<sup>[4-7]</sup>. In the late 1980s, Fu et al.<sup>[8-10]</sup> primarily studied the UV laser induced heterogeneous catalysis polymerization of phenylacetylene (PA) and styrene. High yield and quantum yield of polymer were obtained and the primary dissociation process of  $W(CO)_6$  in  $CCl_4$  was detected by transition IR spectra. The major advantage of UV laser induced catalysis polymerization is that the action of laser is only to produce catalyst in short time and the polymerization of monomer carried out spontaneously in mild conditions. Therefore, the efficiency of photon is largely developed.

On the basis of the previous study on UV laser induced heterogeneous catalysis polymerization, in this paper, we have carried out the UV laser initiated homogeneous catalysis polymerization of PA by  $W(CO)_6-CH_3I$ ,  $W(CO)_6-I_2-C_6H_6$ , and  $W(CO)_6-CHI_3-C_6H_6$  catalyst systems respectively. The

\* To whom correspondence should be addressed

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effects of laser parameters on polymerization of PA, the polymerization mechanism, and the characterization on structure of polyphenylacetylene (PPA) were investigated.

## EXPERIMENTAL

$W(CO)_6$  was purchased from Fluka Chemical Inc. and used without further purification. Phenylacetylene (purity  $\geq 97\%$ ) from Fluka Chemical Inc., was dried over  $CaH_2$  and distilled twice before use.  $CH_3I$  was from Xing Fu Institute of Fine Chemistry, Beijing (Purity  $\geq 98\%$ ), dried over  $CaH_2$  and distilled twice before use.  $I_2$  was from Beijing Chemical Factory (Purity  $\geq 99.8\%$ ),  $CHI_3$  from Shanghai Chemical Factory (Purity  $\geq 99.8\%$ ) was used as received.

UV pulsed laser was double, triple and quadruple frequency of  $Nd^{3+}$ : YAG laser (Quanta-Ray) operating at 532, 355 and 266 nm respectively. Pulse duration is 6ns and repetition rate 10Hz. Experimental process was as follows: UV laser irradiates the solutions of  $W(CO)_6-CH_3I$ ,  $W(CO)_6-I_2-C_6H_6$  and  $W(CO)_6-CHI_3-C_6H_6$  separately degassed with high pure Ar gas. After several minutes of irradiation, the solutions were added to monomer of PA and the mixtures were kept in dark at room temperature for 24 hours. By removing solvent, the polymer was obtained. The photoproducts of  $W(CO)_6$  in various ligands were measured with IR spectrometer (Specord 75). The structure of PPA obtained was measured with IR spectrometer (PE 983G) and  $^1H$  NMR spectrometer (Varian-Unity 200). The molecular weight of PPA was determined by light scattering method.

## RESULTS AND DISCUSSION

### 1. Effect of catalyst on the polymerization of phenylacetylene

Upon the laser photolysis of  $W(CO)_6$ , the  $W(CO)_5$  was first formed and rapidly complexed with entering ligand to form catalyst. Therefore the entering ligands can affect the character of catalyst. The experimental results (in Table 1) show that the catalysts from different catalyst system obviously affect the yield, structure and molecular weight of PPA. Furthermore the catalyst from  $W(CO)_6-CH_3I$  is the most efficient to the polymerization of PA.

Table 1 Synthesis of cis and trans isomer polyphenylacetylene by different catalyst precursors

| Polymer PPA samples | Catalyst precursor     | Yield of polymer | Structure configuration | Molecular weight  |
|---------------------|------------------------|------------------|-------------------------|-------------------|
| 1 <sup>a</sup> PPA  | $W(CO)_6-CH_3I$        | 90%              | Cis                     | $3.9 \times 10^3$ |
| 2 <sup>a</sup> PPA  | $W(CO)_6-I_2-C_6H_6$   | 40%              | Trans                   | $6.0 \times 10^3$ |
| 3 <sup>a</sup> PPA  | $W(CO)_6-CHI_3-C_6H_6$ | 35%              | Trans                   | $1.2 \times 10^4$ |
| 4 <sup>b</sup> PPA  | $W(CO)_6-CCl_4$        | 95%              | Trans                   | $6.6 \times 10^4$ |

Conditions: a) Laser wavelength is 355nm, laser energy 10mJ/p, laser irradiation time 70 minutes, polymerization time 24 hours and repetition rate 10 Hz.  $[W(CO)_6] = 16mM$ ,  $[I_2] = 16mM$ ,  $[CHI_3] = 16mM$  and  $[PA] = 2.3mM$ ; b) Laser wavelength is 355nm, laser energy 4mJ/p, laser irradiation time 50 minutes and polymerization time 24 hours.  $[W(CO)_6] = 10mM$  and  $[PA] = 2.3mM$ .

In fact, the results reflect the strong dependence of activity of catalyst on the

entering ligand. One of the reasons of the effect of entering ligand on the catalyst is that the absorption of incident light by entering ligand decreases the intensity of incident light used for the photolysis of  $W(CO)_6$ . The typical absorption bands of  $W(CO)_6$ ,  $CH_3I$ ,  $I_2$  and  $CHI_3$  separately appear at 255—382, 295, 480—540 and 280—360nm.

Besides, the characteristic of entering ligand is also an important factor for affecting the efficiency of catalyst in the catalysis polymerization of PA.

## 2. Effects of laser parameters on the yield of polyphenylacetylene

By choosing  $W(CO)_6-CH_3I$  as catalyst system, the effects of laser parameters including laser energy, laser irradiation time, lifetime of catalyst and laser wavelength on the yield PPA were investigated.

### (1) Effect of laser energy on yield of PPA

From Fig. 1, it shows that the yield of PPA increases with the increase of laser energy.

### (2) The effect of laser irradiation time on the yield of PPA

As seen from Fig. 2, with the increase of laser irradiation time, the yield of polymer increases and reaches to saturation after 70 minutes.

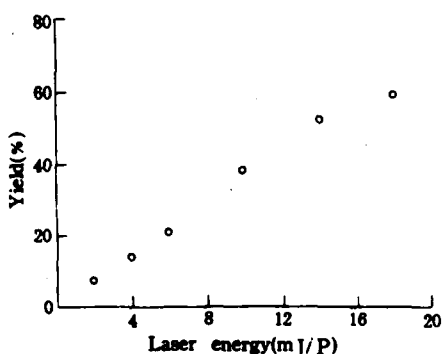


Fig. 1 The dependence of yield of PPA on the laser energy  
Laser irradiation time is 30 minutes, polymerization time 24 hours and repetition rate 10Hz

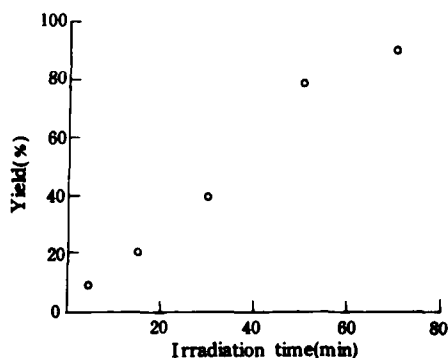


Fig. 2 The dependence of yield of PPA on the laser irradiation time  
Laser energy is 10mJ/p, polymerization time 24 hours and repetition rate 10Hz

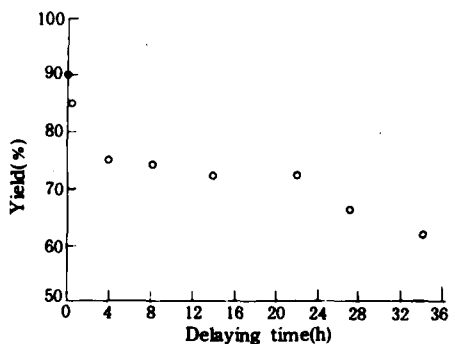


Fig. 3 The dependence of yield of PPA on delaying time of catalyst  
Laser energy is 10mJ/p, laser irradiation time 70 minutes, polymerization time 24 hours and repetition rate 10Hz.

### (3) The effect of lifetime of catalyst on the yield of PPA

The  $W(CO)_6-CH_3I$  was irradiated for 70 minutes, then delayed in dark in a certain time, finally added to the monomer of PA. The dependence of yield of PPA on the delaying time of catalyst is illustrated in Fig. 3 which shows that the catalyst obtained from  $W(CO)_6-CH_3I$  has long lifetime.

### (4) The effect of laser wavelength on the yield of PPA

The photoproducts of  $W(CO)_6$  in  $CH_3I$

produced by irradiation of  $W(CO)_6-CH_3I$  for 50 minutes under 266, 355 and 532nm laser separately were added to the monomer of PA for polymerization. The PPA was obtained only by 355nm laser irradiation  $W(CO)_6-CH_3I$ , whereas no PPA was formed by 266 and 532nm laser irradiation  $W(CO)_6-CH_3I$ . This result indicates that 266 and 532nm laser are ineffective for the polymerization of PA owing to the strong absorption of 266nm incident light by  $CH_3I$  and no absorption of 532nm incident light by  $W(CO)_6$ .

### 3. IR spectra of laser photoproducts of $W(CO)_6$ in $CH_3I$ , $I_2-C_6H_6$ and $CHI_3-C_6H_6$

The photolysis of  $W(CO)_6$  in various ligands were determined by IR spectra as shown in Fig.4. Curve  $A_1$  is the IR spectrum of CO vibration of  $W(CO)_6$  (1mM) appearing at  $1975cm^{-1}$ . Curve  $A_2$  is the IR of CO vibration of photoproduct of  $W(CO)_6$  (1mM) in  $I_2$  (1mM)- $C_6H_6$  irradiated 40 minutes with 355nm laser (10mJ/p, 10Hz), four peaks appearing at 2075, 2000, 1965 and  $1950cm^{-1}$  were observed which are consistent with those of photoproduct of  $W(CO)_6-I_2-C_6H_6$  [11]. Therefore the photoproduct of  $W(CO)_6$  in  $I_2-C_6H_6$  is assigned to  $W(CO)_4I_2$  complex. Curve B is IR spectrum of CO vibration of photoproduct of  $W(CO)_6$  in  $CHI_3-C_6H_6$  irradiated 40 minutes with 355nm laser (10mJ/p, 10Hz). The peaks obtained are consistent with that of photoproduct of  $W(CO)_6$  in  $I_2-C_6H_6$ . Curve C is the IR spectrum of CO vibration of photoproduct of  $W(CO)_6$  (1mM) in  $CH_3I$  irradiated 20 minutes with 355nm laser (10mJ/p, 10Hz). Four peaks were observed at 2075, 2040, 1950 and  $1920cm^{-1}$ . The peaks at 2075, 1950 and  $1920cm^{-1}$  decrease with delaying time, whereas the  $2040cm^{-1}$  increases with the increase of delaying time. Therefore the peaks at 2075, 1950 and  $1920cm^{-1}$  should be assigned to  $A_{1a}$ , E and  $A_{1b}$  mode of CO vibration of  $W(CO)_5L$  and the photoproduct of  $W(CO)_6$  in  $CH_3I$  is  $W(CO)_5CH_3I$ .

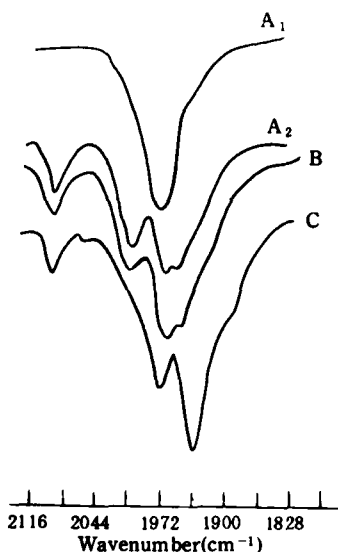


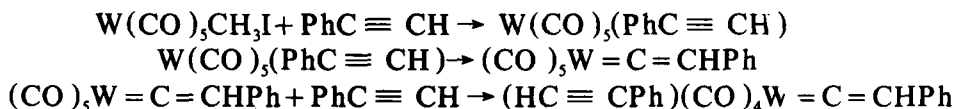
Figure 4. IR spectra of laser photoproducts

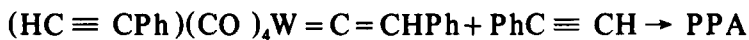
$A_1 - W(CO)_6$ ;  $A_2 - W(CO)_4I_2$ ;  
B -  $W(CO)_4I_2$ ; C -  $W(CO)_5CH_3I$ .

### 4. The polymerization mechanism of PA by $W(CO)_5CH_3I$ and $W(CO)_4I_2$ catalyst

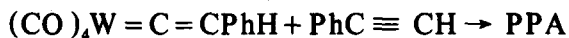
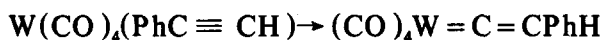
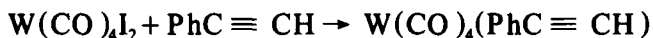
It has been previously shown that the  $W(CO)_5$  and  $W(CO)_4$  species can catalyze the polymerization of alkyne and the polymerization proceeds by a catalytically active vinylidene complexes [12]. The polymerization mechanism of PA by  $W(CO)_5CH_3I$  and  $W(CO)_4I_2$  catalysts are separately demonstrated in scheme I and scheme II.

#### Scheme I





Scheme II



In Scheme I and Scheme II, the initially formed  $\eta^2$ -alkyne complexes are different and thus leads to different structures of PPA.

### 5. The characterization of polyphenylacetylene

In order to elucidate the *cis-trans* structure of PPA, a few structural details have been taken into consideration. The IR spectra of *cis-transoidal* and *trans-cisoidal* PPA are shown in Figure 5(A, B) and present at 634, 740, 890, and 1360 $\text{cm}^{-1}$  the peaks characteristic of *cis-transoidal* structural PPA obtained by  $\text{W}(\text{CO})_5\text{CH}_3\text{I}$  catalyst, while the IR spectrum of *trans-cisoidal* structural PPA obtained by  $\text{W}(\text{CO})_4\text{I}_2$  catalyst are void of these bands and show three characteristic bands at 937 and 1268 $\text{cm}^{-1}$ . Furthermore, for *cis-transoidal* structural PPA, the ratio of 1490 and 1441 $\text{cm}^{-1}$  is smaller than 1, whereas for *trans-cisoidal* structural PPA, the ratio of 1490 and 1441 $\text{cm}^{-1}$  is larger than 1.

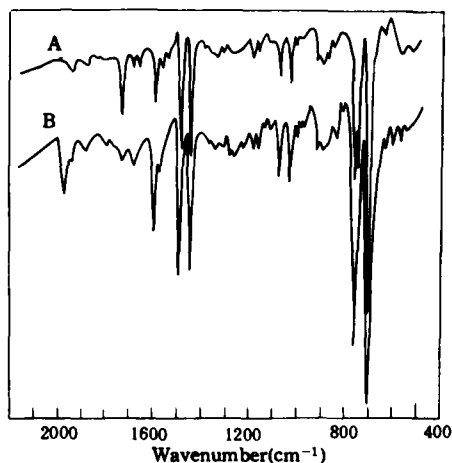


Fig.5 The typical IR spectra of different structural PPA.  
A: *cis-transoidal* structure (85% *cis* content) obtained by  $\text{W}(\text{CO})_5\text{CH}_3\text{I}$ ; B: *trans-cisoidal* structure obtained by  $\text{W}(\text{CO})_4\text{I}_2$

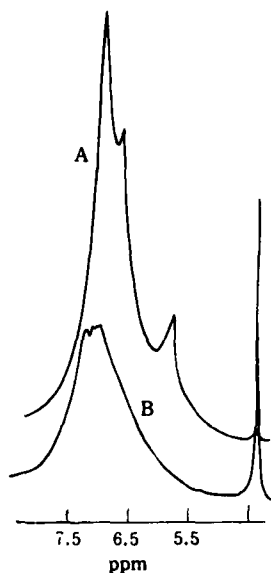


Fig.6 The typical  $^1\text{H}$  NMR spectra of PPA;  
A: *cis-transoidal* structure (85% *cis* content) obtained by  $\text{W}(\text{CO})_5\text{CH}_3\text{I}$ ; B: *trans-cisoidal* structure obtained by  $\text{W}(\text{CO})_4\text{I}_2$

The  $^1\text{H}$  NMR spectra of *cis-transoidal* structural and *trans-cisoidal* structural PPA are shown in Figure 6 (A, B). The  $^1\text{H}$  NMR of *cis-transoidal* structural PPA have three proton resonance centered at  $\delta = 5.82\text{ppm}$  (one *cis* polyenic proton),  $\delta = 6.7\text{ppm}$  (one aromatic proton) and  $\delta = 6.85\text{ppm}$  (four

aromatic protons).

The *cis* content (85%) in *cis-transoidal* PPA was determined from  $^1\text{H}$  NMR spectrum using the area of peak from  $\delta=5.82\text{ppm}$  ( $A_{5.82}$ ) and the total area of the spectrum ( $A_t$ ) according to eq.(1)<sup>[13]</sup>

$$\text{cis}\% = \frac{A_{5.82} \times 10000}{A_t \times 16.66} \quad (1)$$

The  $^1\text{H}$  NMR spectrum of *trans-cisoidal* PPA shows at  $\delta=7.0\text{ppm}$  (the resonance of aromatic monosubstituted protons and *trans*-polyenic protons).

The molecular weight of *cis-transoidal* and *trans-cisoidal* PPA were measured by photo-scattering method (in Table 1), and the molecular weight of *cis-transoidal* PPA is smaller than that of *trans-cisoidal* PPA.

## CONCLUSION

In this paper, we investigated the polymerization of PA by homogeneous catalysts  $\text{W}(\text{CO})_6$ ,  $\text{CH}_3\text{I}$  and  $\text{W}(\text{CO})_6\text{I}_2$ . The *cis-transoidal* PPA catalyzed by  $\text{W}(\text{CO})_6\text{CH}_3\text{I}$  shows lower molecular weight than that of *trans-cisoidal* PPA. Combining with the polymerization of PA by the catalyst from the photoproduct of  $\text{W}(\text{CO})_6$  in  $\text{CCl}_4$ , we note that the photoproducts of  $\text{W}(\text{CO})_6$  in various halocarbon ligands ( $\text{CCl}_4$ ,  $\text{CH}_3\text{I}$ ,  $\text{I}_2$  and  $\text{CHI}_3$ ), used as catalyst, can stereoselectively catalyze the polymerization of PA.

## Keywords:

UV laser initiation; Polyphenylacetylene; Homogeneous catalysis polymerization.

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