

Simultaneous Polymerization and Formation of Poly(propargyl alcohol) Films by a Novel Palladium Catalyst

Mujie YANG, Hongmei SUN, and Weiguo CHEN*

Department of Polymer Science and Engineering, Zhejiang University,
Hangzhou 310027, China

* Department of Chemistry, Hangzhou University, Hangzhou 310013, China

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ABSTRACT: Simultaneous polymerization and formation of poly(propargyl alcohol) (POHP) films by $[\text{Pd}(\text{C}\equiv\text{CCH}_2\text{OH})_2(\text{PPh}_3)_2](\text{Pd}-\text{C})$ catalyst in $\text{CH}_2\text{Cl}_2-\text{CCl}_4$ mixed solvent system have been investigated. Some features and kinetic behavior for the OHP polymerization are described and discussed. The overall polymerization activation energy was found to be 76.4 kJ mol^{-1} and the rate equation can be expressed as $R_p = k_p[\text{OHP}][\text{Pd}-\text{C}]$, where $k_p = 1.32 \times 10^{-3} \text{ L mol}^{-1} \text{ s}^{-1}$ (58°C). The POHP polymer obtained is a black sheeny film stable in air and chlorinated by $\text{CH}_2\text{Cl}_2-\text{CCl}_4$ mixed solvent. Its conducting properties were investigated.

KEY WORDS Propargyl Alcohol / Bis(triphenylphosphine)-Bis(2-propynyl-1-ol)palladium Catalyst / Polymerization / Poly(propargyl alcohol) Film /

Since Shirakawa *et al.*¹ succeeded in synthesizing a uniform and free standing film of polyacetylene by a direct method in 1974, there have been many studies on polyacetylene.² Particularly, doped polyacetylene shows the metallic conductivity, which has received a great deal of attention in the past years. However, polyacetylene is unstable in air and insoluble in the usual organic solvents. Thus, though the electrical conductivity is somewhat low, the synthesis and properties of substituted polyacetylene have been intensively investigated.³ Poly(propargyl alcohol) (POHP) is one of them. But, there was no much satisfaction with the results of the synthesis of POHP in the past 30 years.⁴⁻⁵ Recently, we reported that a bis(triphenylphosphine)-bisacetylide palladium complex $\text{Pd}(\text{C}\equiv\text{CCH}_2\text{OH})_2(\text{PPh}_3)_2(\text{Pd}-\text{C})$ is a novel effective catalyst for the OHP homogeneous polymerization in $\text{CHCl}_3-\text{CH}_3\text{OH}$ mixed solvent system at 60°C .⁷ In the present paper we report further research results on simultaneous polymerization and formation of POHP

film with Pd-C catalyst in $\text{CH}_2\text{Cl}_2-\text{CCl}_4$ mixed solvent system at about 60°C , which in turn is a development based upon our previous work on the acetylene, phenylacetylene polymerization.^{8,9}

EXPERIMENTAL

Materials

Propargyl alcohol (OHP), 2-propynyl-1-ol, was distilled under nitrogen at reduced pressure. All the reagents (palladium chloride, cuprous iodide, diethylamine, triphenylphosphine, and ferric chloride anhydrous, etc.) were analytical or chemical grade. *trans*-Bis(triphenylphosphine) dichloropalladium $\text{PdCl}_2(\text{PPh}_3)_2$ was prepared by a classical method. A typical reaction procedure is given here: 0.1400 g of PdCl_2 , 0.0944 g of NaCl dissolved in small amount of water, and 300 ml of ethanol were added to a 1000 ml reaction flask. The mixture was maintained under stirring at 50°C for about 4 h, then filtered. An ethanol solution containing 0.4142 g of PPh_3 was

added to the filtrate. The reaction mixture was stirred at 50°C for about 10 min. The yellow precipitate formed was separated by filtration, washed with warm ethanol, then dried *in vacuo*, yield about 85%. The UV spectrum in CHCl_3 of $\text{PdCl}_2(\text{PPh}_3)_2$ exhibits a maximum at 216.8 nm. *Anal.* Calcd for $\text{Pd}(\text{Cl}_2\text{P}_2\text{C}_{36}\text{H}_{30})$: C, 61.60%; H, 4.28%, Found: C, 61.48%; H, 4.27%.

The complex $[\text{Pd}(\text{C}\equiv\text{CH}_2\text{OH})_2(\text{PPh}_3)_2]$ (Pd-C) was prepared as previously reported.⁷

Polymerization

All procedures for polymerization were carried out under purified nitrogen atmosphere. A typical polymerization procedure is as follows: into a 30 ml well-dried ampoule, Pd-C as the catalyst, CH_2Cl_2 and CCl_4 were added in turn, shaken and/or heated (<60°C) to obtain a homogeneous solution, and then propargyl alcohol (OHP) was injected. After the mixture stood at 58°C for a definite reaction time, a black sheeny polymer (POHP) film was formed, the filtered, washed with hexane, chloroform-ethanol mixed solvent, ethanol in this order, and dried at room temperature under vacuum for about 8 h. The polymer yield was calculated by gravimetry.

Doping

POHP was doped by dipping the film into a solution of I_2 in hexane, or of I_2 in dichloromethane, or of FeCl_3 in nitromethane, or of H_2SO_4 in tetrahydrofuran. After a definite time, the solvent was eliminated under vacuum. The residue was repeatedly washed with solvents used in the doping procedure and then dried in vacuum at room temperature. The doping levels were determined by the weight uptake method.

Measurements

Infrared (IR) spectra were recorded on a Nicolet 5-DX FTIR with a KBr pellet. The elemental analyses were carried out by a Carloerba Model 1106 elemental analyzer.

Electron spin resonance (ESR) measurements were taken on a JES-FEIXG ESR spectrometer. Ultraviolet (UV) spectra were recorded on a Shimadzu UV 240 spectrometer. Electrical resistivities were measured by the high-resistance meter (mod. ZC36), and carried out at room temperature on the pellets compressed at 600 kg cm^{-2} . The chlorinity of POHP polymer was detected by oxygen flask method.

RESULTS AND DISCUSSION

Features of OHP Polymerization with $\text{Pd}(\text{C}\equiv\text{CCH}_2\text{OH})_2(\text{PPh}_3)_2$ Catalyst

The $\text{Pd}(\text{C}\equiv(\text{CH}_2\text{OH})_2(\text{PPh}_3)_2(\text{Pd}-\text{C}))$ is a novel catalyst for the polymerization of propargyl alcohol (OHP).⁷ Solvent system is a key factor for simultaneous polymerization and formation of POHP films and greatly influences the polymerization activity. In general, simultaneous polymerization and formation of polymer films easily carry out in a mixed solvent system consisted of solvent and non-solvent of the polymer. It was found that the OHP could polymerize with Pd-C catalyst in the solvent systems that follow: CCl_4 , CHCl_3 - CH_3OH , CHCl_3 - CCl_4 , CH_2Cl_2 - CCl_4 , $\text{C}_2\text{H}_5\text{OH}$ - CCl_4 , and toluene- CCl_4 . Of all the solvent systems, however, CH_2Cl_2 - CCl_4 mixed solvent is a favorable one for simultaneous polymerization and formation of POHP film, while the conversion for the OHP polymerization reached 90% under the tested conditions. The effect of CCl_4 concentration $[\text{CCl}_4]$ on the conversion of POHP films is shown in Figure 1. With increasing the CCl_4 concentration up to 5 mol L^{-1} , the polymerization conversion increases. In fact, for obtaining high quality of POHP films, the optimum CCl_4 concentration is 3.10 mol L^{-1} , that is, the volume ratio of $\text{CH}_2\text{Cl}_2/\text{CCl}_4$ is 1 ($V_C/V_T=1$), both above and below this concentration, the POHP films obtained were not good.

The Pd-C complex is also an effective catalyst for OHP polymerization in CH_2Cl_2 -

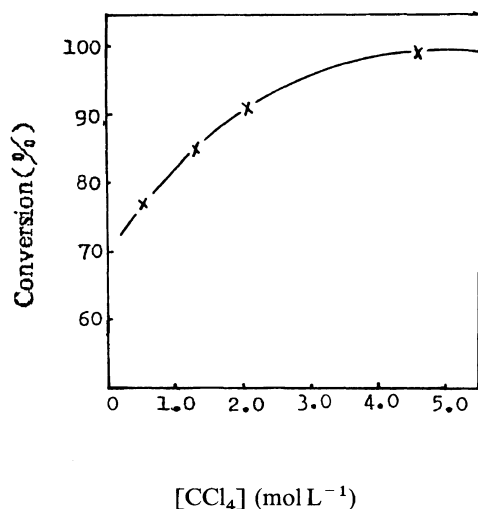


Figure 1. Effect of CCl_4 concentration $[\text{CCl}_4]$. Conditions: $\text{CH}_2\text{Cl}_2\text{-CCl}_4$ solvent system; $[\text{Pd-C}] = 3.0 \times 10^{-2} \text{ mol L}^{-1}$; $[\text{OHP}] = 6.8 \text{ mol L}^{-1}$; N_2 ; 58°C and 24h.

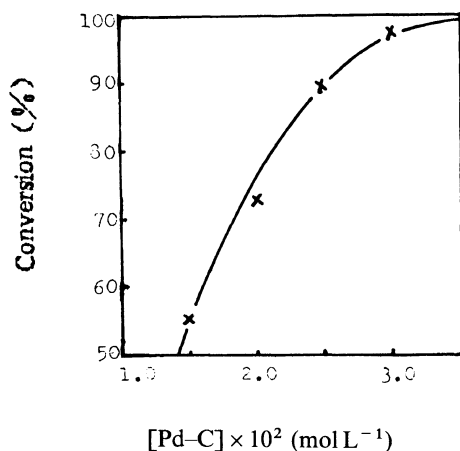


Figure 2. Effect of catalyst concentration $[\text{Pd-C}]$. Conditions: $\text{CH}_2\text{Cl}_2/\text{CCl}_4 = 1$ (volume ratio), others are the same as in Figure 1.

CCl_4 mixed solvent system at 58°C . The effect of catalyst Pd-C and monomer OHP concentration, and polymerization temperature on the OHP polymerization are illustrated in Figures 2, 3, and 4. It is seen that the conversion for the OHP polymerization increases rapidly with increasing catalyst concentration and polymerization temperature, and de-

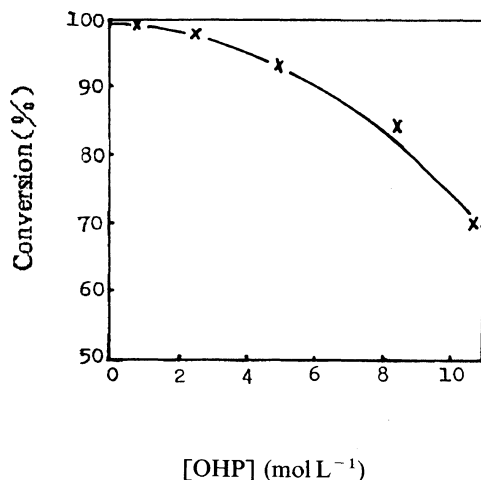


Figure 3. Effect of monomer concentration $[\text{OHP}]$. Conditions: $\text{CH}_2\text{Cl}_2/\text{CCl}_4 = 1$ (volume ratio), others are the same as in Figure 1.

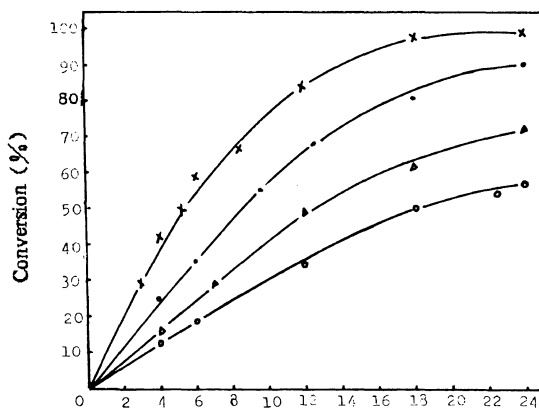


Figure 4. Time-conversion curves for the OHP polymerization at different temperature, T , $^\circ\text{C}$: (○) 45; (△) 50; (●) 55; (×) 58. Conditions: $\text{CH}_2\text{Cl}_2/\text{CCl}_4 = 1$ (volume ratio), others are the same as in Figure 1.

creases with increasing monomer concentration. For combination of high conversion and obtaining better POHP films, the optimum catalyst and monomer concentration, and polymerization temperature are considered $3.0 \times 10^{-2} \text{ mol L}^{-1}$ of Pd-C, 6.8 mol L^{-1} of OHP, and 58°C , respectively, under the tested conditions ($V_C/V_T = 1$, after 12 h polymerization).

Kinetic Behavior of Polymerization

The kinetic behavior of simultaneously polymerizing and forming of POHP films with the Pd-C catalyst in $\text{CH}_2\text{Cl}_2\text{-CCl}_4$ mixed solvent system at 58°C has been studied. It is seen from Figure 4 that the conversion increases linearly up to 6 h, and subsequently levels off. The apparent polymerization rate (R_p) at different catalyst concentrations [Pd-C] was calculated from the conversion measured in the initial stage at constant monomer concentration [OHP] = 6.8 mol L^{-1} . Figure 5 is the plot of $\log R_p$ vs. $\log[\text{Pd-C}]$ and indicates that $\log R_p$ is in a linear relationship with $\log[\text{Pd-C}]$ having a slope of approaching 1, i.e., the polymerization reaction is of first order with respect to catalyst concentration [Pd-C]. Figure 6 shows some polymerization times versus $-\ln(1-c)$ curves at different [Pd-C]. From Figure 6 it is clear that the polymerization reaction is of first order with respect to monomer concentration [OHP] under the catalyst concentration tested. Thus the polymerization rate equation can be written as:

$$R_p = k_p[\text{OHP}][\text{Pd-C}]$$

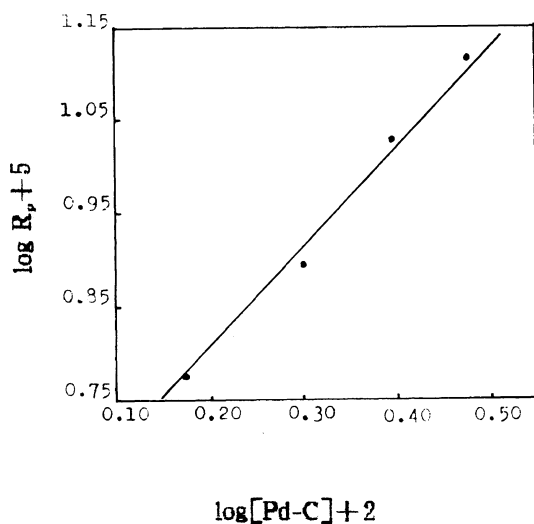


Figure 5. Plot of $\log R_p$ vs. $\log[\text{Pd-C}]$. Conditions: $\text{CH}_2\text{Cl}_2/\text{CCl}_4 = 1$ (volume ratio), $[\text{OHP}] = 6.8 \text{ mol L}^{-1}$, N_2 , and 58°C .

where k_p is the apparent polymerization rate constant, equal to $1.32 \times 10^{-3} \text{ L mol}^{-1} \text{ s}^{-1}$ (58°C).

Figure 7 shows the influence of polymerization temperature and indicates an Arrhenius-type dependence. Thus, the overall activation energy of OHP polymerization with Pd-C catalyst was found to be 76.4 kJ mol^{-1} .

Besides, it was observed that the OHP polymerization was not suppressed by in-

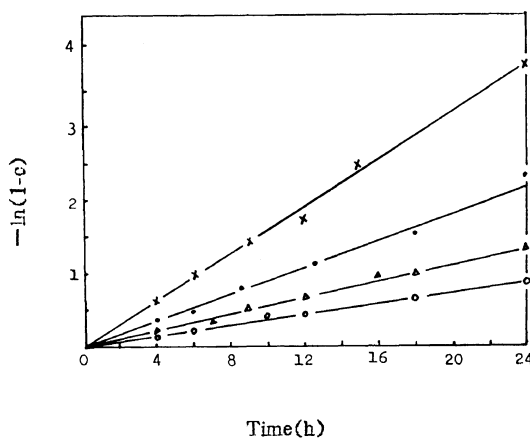


Figure 6. Reaction time vs. $-\ln(1-c)$ curves for the OHP polymerization at different catalyst concentration. [Pd-C], mol L^{-1} : (x) 3.0×10^{-2} ; (●) 2.5×10^{-2} ; (Δ) 2.0×10^{-2} ; (○) 1.5×10^{-2} . Conditions are the same as in Figure 5.

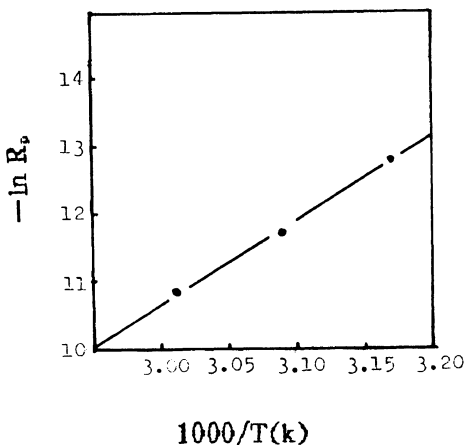


Figure 7. Arrhenius plot of the rate of polymerization (R_p) vs. temperature. Conditions: $\text{CH}_2\text{Cl}_2/\text{CCl}_4 = 1$ (volume ratio); $[\text{Pd-C}] = 3.0 \times 10^{-2} \text{ mol L}^{-1}$; $[\text{OHP}] = 6.8 \text{ mol L}^{-1}$, N_2 .

corporation of hydroquinone in the medium, and was accelerated by adding a solution of FeCl_3 in *N,N*-dimethylformamide (DMF) to the polymerization system. Moreover, no free radical signal was detected while dynamic tracing the OHP polymerization with ESR. Combining the above experimental facts, it can be seen that the OHP polymerization with Pd-C catalyst in $\text{CH}_2\text{Cl}_2\text{-CCl}_4$ mixed solvent system at 58°C is probably not free radical polymerization. Precise investigation on the polymerization mechanism will be continued.

Characterization and Doping of Polymer

Poly(propargyl alcohol)(POHP) so prepared by Pd-C catalyst in $\text{CH}_2\text{Cl}_2\text{-CCl}_4$ mixed solvent system at 58°C is a black sheeny film. It is insoluble in most organic solvents, but soluble partially in DMF. The infrared spectra of POHP films obtained (Figure 8) show the characteristic absorption peak of conjugated C=C bonds (1655 cm^{-1}), of CH_2OH groups (1025 cm^{-1}), while the monomeric triple bond (C≡C) peak at 2120 cm^{-1} is missing. The UV analysis of POHP film revealed an absorption maximum (in DMF) at 356.5 nm , which indicated forming a π -conjugated chain.

The POHP polymer is stable in air. No noticeable weight uptake and no remarkable change in IR spectra (Figure 8) were examined with storage time.

Preliminary conductivity measurements of the POHP films doped with I_2 /hexane, I_2 /dichloromethane, FeCl_3 /nitromethane, and H_2SO_4 /tetrahydrofuran gave values of about 5.9×10^{-9} , 2.1×10^{-9} , and $2.1 \times 10^{-8}\text{ s cm}^{-1}$, respectively, which increased by 3–4 orders of magnitude as compared to the undoped POHP film.

It is worth noting that the POHP films obtained were chlorinated by $\text{CH}_2\text{Cl}_2\text{-CCl}_4$ mixed solvent in the polymerization process, which is confirmed by the IR spectra and Cl-content measurements of the POHP films. Characteristic absorptions of C-Cl bond (750 and 790 cm^{-1}) indicating a chlorine containing

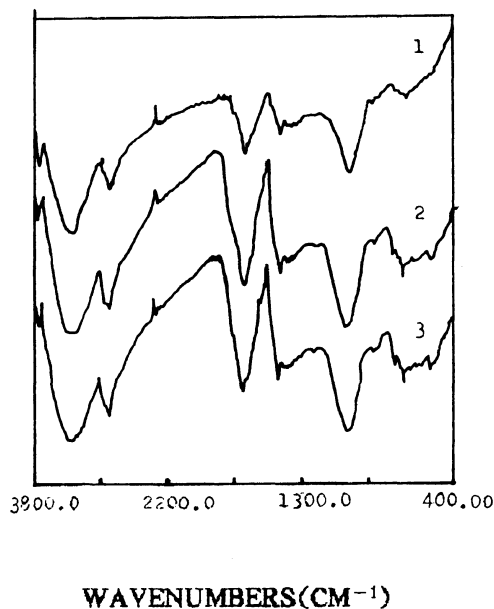


Figure 8. Infrared spectra of POHP films in different atmosphere at room temperature for 7 days: (1) in N_2 ; (2) in air; (3) in vacuum.

of POHP films were observed in the IR spectra (Figure 8). The Cl-content analysis revealed that the Cl-content of the POHP film obtained under the experimental conditions is about 13 wt%, and increases with increasing mole ratio of $\text{CH}_2\text{Cl}_2\text{-CCl}_4$ mixed solvent to monomer OHP. The above results indicated that, perhaps, this POHP polymer could be used as a resistance-burning conductive material. Further investigations are in progress.

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