

STUDIES ON THE CATALYTIC BEHAVIORS OF SOME BIPOLYMER—PALLADIUM COMPLEXES FOR HYDROGENATION OF NITRO-COMPOUNDS AND OLEFINS

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ABSTRACT

Some water-soluble bipolymer-Pd complexes were prepared. It was found that the bipolymer-Pd complexes exhibited remarkably higher catalytic activity and stability than that of the single polymer-Pd complex for hydrogenation of nitro-compounds and olefins under mild conditions.

INTRODUCTION

In recent years, many studies on polymeric catalyst have been reported^[1,2]. Polymeric catalysts have several advantages such as high catalytic activity, selectivity and stability. In general, the polymer supporters used for polymeric catalysts consists of only one kind of polymer. It is well known that natural polymeric catalyst, such as enzyme, has extremely high activity and selectivity under mild conditions. However, the enzyme consists of several kinds of polymers, whether it has metal ion or not. It is obvious that the catalytic properties of enzyme are greatly affected by the interaction between the peptide chains^[3]. Therefore, we have focused our attention on the effects of the interaction between two or more kinds of synthetic polymers in polymeric catalyst.

Interpolymer complex is formed due to the secondary binding forces between different polymer chains such as hydrogen bond, coulomb force, van der Waals force and charge-transfer interaction^[4]. These interactions between two kinds of polymer not only affect the metal complex centre and reaction fields, but also affect the catalytic behaviors in the polymeric catalyst.

In this paper, some of bipolymer-Pd complexes were synthesized and their catalytic properties for hydrogenation of nitro-compounds and olefins were investigated. It was found that the bipolymer-Pd complexes has remarkably higher catalytic activity and stability than that of single polymer-Pd complex.

EXPERIMENTAL

Water-soluble polymers, polyacrylic acid (PAA, $\bar{P}_n=8400$)^[5], polymethacrylic acid (PMAA, $\bar{P}_n=2670$)^[6], poly(styrene-maleic anhydride) (PSM)^[7], polystyrene sulfonic acid (PSSA, $\bar{M}=110,000$, $-\text{SO}_3\text{H}=92\%$)^[8] and polyacrylamide (PAAm, $\bar{M}=122,000$)^[9], were

prepared as literature related.

Copolymer of styrene and maleic acid with diethylamide group (PSM-NEt₂): Poly(styrene-maleic anhydride) 5.0g and excess diethylamine were mixed under stirring at 30–40°C for about 10 hr, the reaction product was separated, washed with benzene, dried in vacuum. Yield 4.3g.

Elemental analysis: C 61.60%; H 7.59%; O 17.31%; N 4.81%. the degree of ammonolysis=94%.

Copolymer of styrene and maleic acid with amide group (PSM-NH₂) and copolymer of styrene and maleic acid (PSM) were prepared as PSM-NEt₂, in which the diethylamine was substituted by NH₄OH or NaOH.

Bipolymer-Pd complexes

Methanol solution of polystyrene sulfonic acid (0.05mol/l), polyacrylic acid (0.05mol/l) and PdCl₂·2H₂O (0.05mmol/l) were mixed and stirred at 60°C for 2 hr. The color of the solution is changed from light yellow to brown. The product obtained is abbreviated to PSSA-Pd-PAA complex. In the same way, PSSA-Pd-PMAA, PSSA-Pd-PSM, PSSA-Pd-PSM-NEt₂, PSSA-Pd-PSM-NH₂ and PSSA-Pd-PAAm complexes were also prepared.

Hydrogenation of nitro-compounds or olefins

The bipolymer-Pd complex containing 0.025 mg atom Pd, solvent (25 ml) and substrate (0.015 mol) were added to the glass reactor with a gas inlet tube, an outlet tube and water jacket. The reactor was placed on a vibrator and fixed with hydrogen storage bottle. The constant temperature water was passed through the jacket from a water bath. The system was alternately evacuated and flushed with hydrogen for three times. The reaction solution was vibrated and the volume of hydrogen uptake was measured at 1 atm. hydrogen pressure. The reaction products were analysed by GLC.

RESULTS AND DISCUSSION

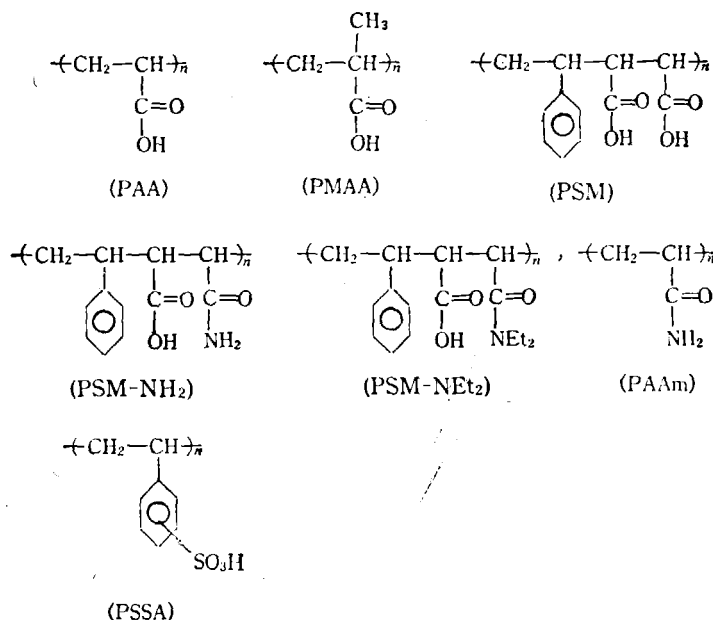
The soluble polymers used are polyacrylic acid (PAA), polymethacrylic acid (PMAA),

Table 1 X-ray photoelectron spectroscopy of the bipolymer-Pd complexes*

	Binding energy (eV)		
	N _{1s}	O _{1s}	Pd _{3d_{5/2}}
PdCl ₂ ·2H ₂ O			338.8
PSSA		532.5	
PSM-NH ₂	400.1	532.5	
PSSA-Pd-PSM-NH ₂	401.1	532.7	338.2
PAA		531.7	
PSSA-Pd-PAA		532.1	338.2

* Using C_{1s} as the inner standard.

poly(styrene-maleic acid) (PSM), copolymer of styrene and maleic acid with amide group (PSM-NH₂), copolymer of styrene and maleic acid with diethylamide group (PSM-NEt₂), polyacrylamide (PAAm) and polystyrene sulfonic acid (PSSA):



These bipolymer-Pd complexes prepared are classified to two systems of polystyrene sulfonic acid (PSSA)—polycarboxylic acid and polystyrene sulfonic acid (PSSA)—polycarboxylic acid with amide group or polyamide.

The X-ray photoelectron spectroscopy of the bipolymer-Pd complexes is shown in Table 1. Compare the bipolymer-Pd complexes with single polymer and PdCl₂·2H₂O, it is clear that the binding energy of N_{1s} was increased by 1.0 eV, that of O_{1s} were increased by 0.4 and 0.2 eV, and that of Pd_{3d 5/2} was decreased by 0.6 eV. And the binding energy of other element were hardly changed for the bipolymer-Pd complexes. The results of this X-ray photoelectron spectroscopy clearly demonstrated that the O→Pd coordination bond and N→Pd coordination bond in bipolymer-Pd complexes are formed.

The relationships between the pH values of solution of bipolymer-Pd complexes and molar ratios of monomeric units of PSSA to Pi (other polymers) in PSSA-Pd-Pi are shown in Figure 1. From the figure, the pH values of solution of the bipolymer-Pd complexes are lower than the pH average values of two single polymer-Pd complexes. The enhance of dissociation of hydrogen ion may be attributed to the hydrogen bond interaction of the interpolymer. This experimental results show that the hydrogen bond between two different polymer chains is formed.

The catalytic behaviors of this bipolymer-Pd complexes for hydrogenation of nitrobenzene are investigated. The relationship between the hydrogenation rate and the molar ratio of two kinds of polymer unit in the complexes of PSSA-Pd-polycarboxylic acid is shown in Fig. 2(a) and that in the complexes of PSSA-Pd-polycarboxylic acid with amide group or polyamide

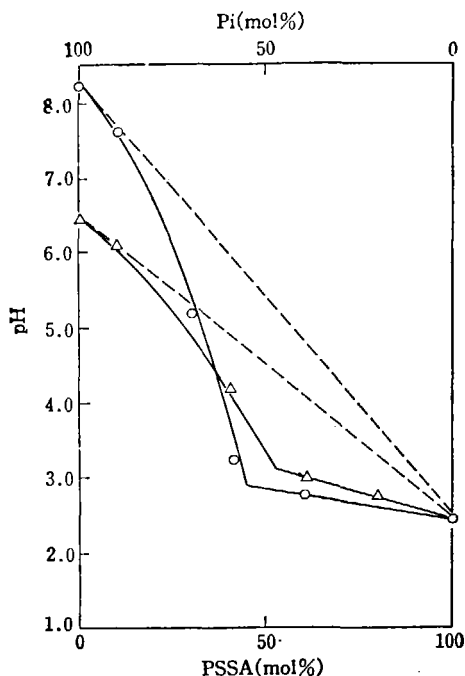


Fig. 1 Relationships between the pH and the molar ratios of monomeric units of PSSA to Pi (other polymers) in PSSA-Pd-Pi
Pd, 0.001 atom/l; PSSA + Pi, 0.01 mol/l.
○ PSSA-Pd-PSM; △ PSSA-Pd-PSM-NH₂.

is shown in Fig. 2 (b). From Fig. 2, it is clear that the catalytic activity of bipolymer-Pd complexes is much higher than that of single polymer-Pd complexes. For example, the hydrogenation rate of nitrobenzene catalyzed by PSSA-Pd-PMAA is raised five times higher than that of PMAA-Pd. It is noteworthy that most of the curves look like "humps" have two peaks respectively. When the molar ratio of monomeric unit of two polymers in the complex is nearly 1:1, the catalytic activity is somewhat lower than the maximum value. However, the catalytic activity of PSSA-Pd-PAAm complex is only slightly higher than that of single polymer-Pd complexes. And the curve of the catalytic activity does not appear the "valley", because the interaction between PSSA and PAAm is weak. Therefore, these catalytic behaviors of bipolymer-Pd complexes are related to the interaction between the two kinds of polymers. In addition, the neighboring organic group (such as methyl, carboxy or amide group) of the carboxylic acid group in the polymer also affect the catalytic behaviors of bipolymer-Pd complex.

Using PSSA-Pd-PSM-NEt₂ complex as catalyst, the hydrogenation for nitro compounds and olefins are investigated. The relationship between the hydrogenation rate for nitrobenzene or p-nitroaniline and the molar ratios of monomeric units of PSSA to PSM-NEt₂ in PSSA-Pd-PSM-NEt₂ complex is shown in Fig. 3 (a). In this figure, we can see that the single polymer-Pd complex, PSSA-Pd or PSM-NEt₂-Pd, have lower catalytic activity of

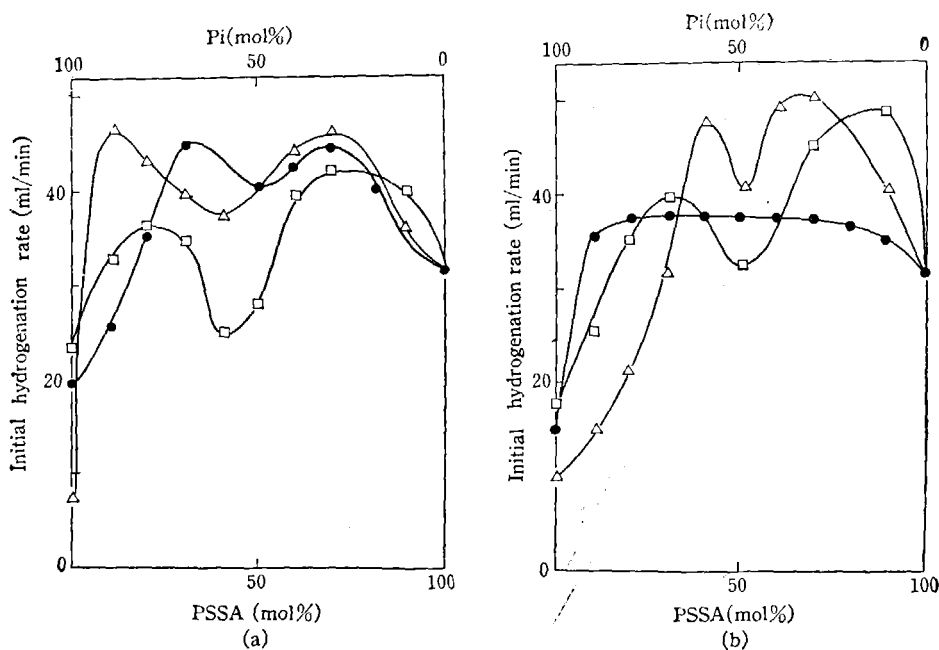


Fig. 2 Relationships between the initial rate of hydrogenation of nitrobenzene and the molar ratios of monomeric units of PSSA to Pi (other polymers) in PSSA-Pd-Pi
Pd, 0.025 mg atom; PSSA+Pi, 0.1 mmol; PhNO_2 , 0.015 mol; Solvent, methanol or methanol-water (10:1); Total reaction volume, 25 ml; 30°C, 1 atm. of hydrogen.

(a) ● PSSA-Pd-PAA
□ PSSA-Pd-PSM
△ PSSA-Pd-PMAA

(b) ● PSSA-Pd-PAAm
△ PSSA-Pd-PSM- NEt_2
□ PSSA-Pd-PSM- NH_2

hydrogenation for p-nitroaniline, however, the maximum catalytic activity of bipolymer-Pd complex, PSSA-Pd-PSM- NEt_2 , is six times as high as single polymer-Pd complex. It is noteworthy that the curve of the relationship between the catalytic activity and the molar ratios of monomeric units of PSSA to PSM- NEt_2 in PSSA-Pd-PSM- NEt_2 complex for the hydrogenation of nitrobenzene looks like "hump", yet that for the hydrogenation of p-nitroaniline is a "parabola". The rate of hydrogenation appears a maximum when the molar ratio of monomeric unit of PSSA to PSM- NEt_2 in this complex is nearly 1:1. Fig. 3 (b) shows the relationships between the rate of hydrogenation for different olefins and component of PSSA-Pd-PSM- NEt_2 complex. It is evident that the different functional groups in the olefin derivatives obviously affect the shape of curves of catalytic activity. Some curves are assumed to have "humps" and other curves look like parabola.

The experimental results mentioned above exhibited that the catalytic behavior of bipolymer-Pd complex, PSSA-Pd-PSM- NEt_2 , is influenced remarkably by the substrates and it may be attributed to the interaction between the bipolymer-Pd complex and the substrates.

We also investigated the catalytic hydrogenation behaviors of PSSA-Pd-PSM- NEt_2 complex for various unsaturation compounds. The hydrogenation behaviors of some single

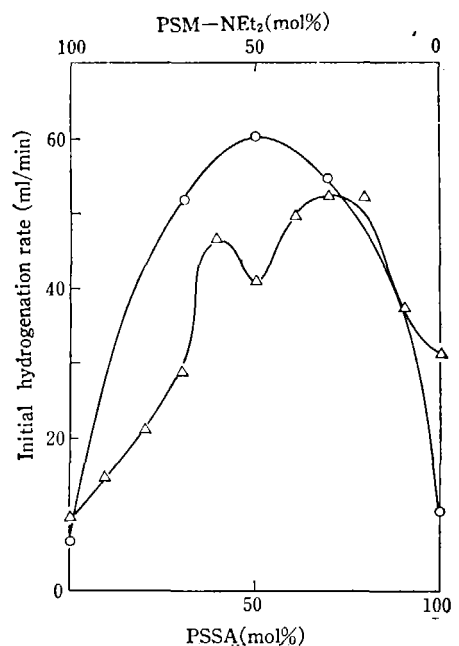
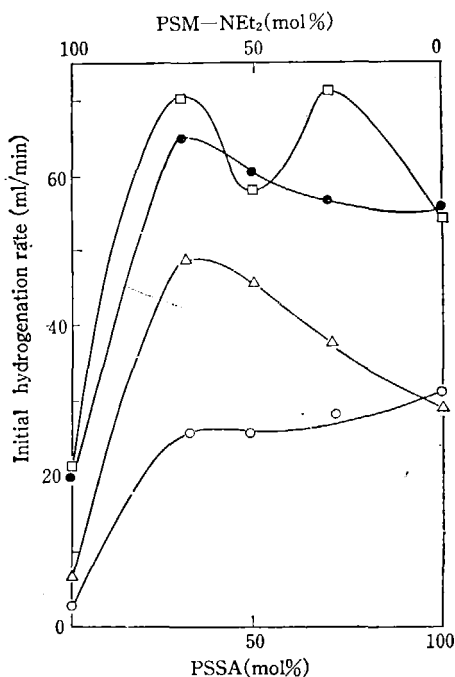
(a) Δ Nitrobenzene; $\circ$ p-nitroaniline.(b) $\square$ Acrylic acid; $\bullet$ Acrylamide; Δ Acrylonitrile; $\circ$ Methacrylic acid.

Fig. 3 Relationships between the initial rate of hydrogenation and the molar ratios of monomeric units of PSSA to PSM-NEt₂ in PSSA-Pd-PSM-NEt₂ complex
 Pd, 0.025 mg atom; PSSA + PSM-NEt₂, 0.1 mmol; Substrate, 0.005 mol; Solvent, methanol; Total reaction volume, 25 ml; 30°C, 1 atm. of hydrogen.

polymer-supported metal complexes, such as Pd complex of polymethacrylic acid^[10], Pd complex of polyvinyl pyrrolidone^[11] and Pd complex of styrene-maleic acid copolymer^[12], for nitro compounds have been reported elsewhere. The hydrogenation activities of bipolymer-Pd complex, PSSA-Pd-PSM-NEt₃, for various nitro compounds are tabulated in Table 2. From Table 2, it is clear that the bipolymer-Pd complex for some aromatic nitro compounds has higher catalytic activity than these single polymer-supported metal complexes^[10-12]. For the aromatic nitro compounds, the substituents of nitrobenzene derivatives obviously affect the hydrogenation rates. The order of hydrogenation activity is that: $-\text{NH}_2 < -\text{CH}_3 < -\text{OH}$. And the locations of the substituents also remarkably affect the hydrogenation rate. For example, the hydrogenation activity increases in the following order: *ortho*- < *meta*- < *para*-, owing to the steric effect of substituent.

Table 2 Hydrogenation rate of PSSA-Pd-PSM-NEt₃ for different nitro compounds

Substrates	Hydrogenation rate (ml/min)
Methyl cyanide	2.0
nitrobenzene	44.2
<i>o</i> -nitroaniline	5.5
<i>m</i> -nitroaniline	44.7
<i>p</i> -nitroaniline	58.8
<i>o</i> -nitrotoluene	24.0
<i>p</i> -nitrotoluene	74.0
<i>o</i> -nitrobenzoic acid	54.5
<i>p</i> -nitrobenzoic acid	69.8
<i>o</i> -nitrophenol	82.2

Reaction conditions are the same as Fig. 3.

The hydrogenation activity of bipolymer-Pd complex, PSSA-Pd-PSM-NEt₃, for various olefins is shown in Table 3. The hydrogenation rate for olefins containing various organic groups increases in the following order: $-\text{CH}_2\text{OH} < -\langle \bigcirc \rangle < -\text{CN} < -\text{COOH} < -\text{CONH}_2$. The influence of the substituents on the hydrogenation of olefins may be attributed to the effect of the substituents on the double bond and may be related to the interaction between the substituents and the bipolymer-Pd complex. The olefins containing carboxylic acid, amide and cyano groups have higher rate of hydrogenation, because the interactions between the bipolymer-Pd complex and these groups are stronger. The hydrogenation rate of allyl alcohol is lower, owing to the fact that the solvent, methanol, screens the interaction between bipolymer-Pd complex and hydroxyl group in the allyl alcohol. Therefore, the interaction between the bipolymer-Pd complex and substrate can affect the catalytic activity. Also the steric effect may impede the process of hydrogenation, for example, the hydrogenation rate of methacrylic acid was only half of that of acrylic acid.

Table 3 Hydrogenation rate of PSSA-Pd-PSM-NEt₃ for different olefins

Substrates	Hydrogenation rate (ml/min)
Acrylic acid	59.1
Methacrylic acid	28.1
*Acrylamide	46.2
Acrylonitrile	55.0
Styrene	41.1
Allyl alcohol	7.1
1-heptene	57.0
Cyclohexene	35.7
Cyclopentadiene	44.0

Substrates, 0.02 mol (*0.005 mol). Other reaction conditions are the same as Fig. 3.

When the molar ratio of monomeric unit of two polymers in the complex is maintained at 1:1, and the quantity of PdCl₂·2H₂O is equal to 0.025×10^{-3} mole. The effects of the ratio of the total monomeric units of two polymers to Pd on the rate of initial hydrogen uptake are shown in Fig. 4. As seen from Fig. 4, the different bipolymer-Pd complexes have different

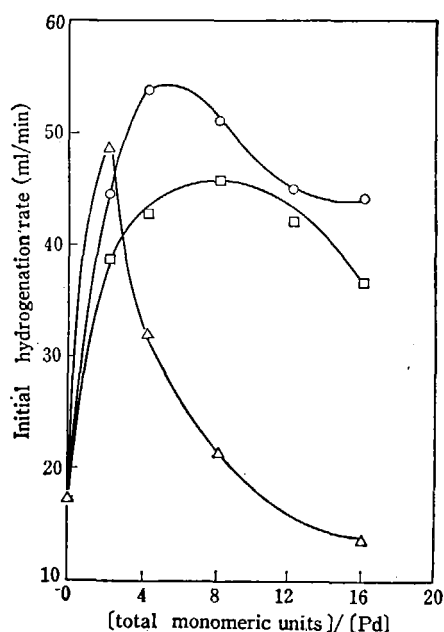


Fig. 4 Relationships between the hydrogenation rate and the [total monomeric units]/[Pd] in the bipolymer-Pd complexes
 PSSA: Pi=1:1, other conditions are the same as Fig. 2.
 △ PSSA-Pd-PSM; ○ PSSA-Pd-PAA; □ PSSA-Pd-PSM-NEt₃.

optimum ratio of the total monomeric units to Pd, in which the catalytic activity reaches maximum. The experimental results mentioned above exhibited that the catalytic activity of the bipolymer-Pd complexes is influenced markedly by the components of them.

The effects of the reaction temperature on the hydrogenation of nitrobenzene by using PSSA-Pd-PAA is also investigated as shown in Fig. 5. The optimum reaction temperature is about 40°C. At temperature higher than 40°C the rate of hydrogenation decreases, because the interaction force of hydrogen bond between the two polymers is weakened, and the vapor of methanol to prevent the contact hydrogen with substrate and catalyst.

The catalytic stability of the bipolymer-Pd complex is shown in Fig. 6. It can be seen that the bipolymer-Pd complex is more stable than that of single polymer-Pd complexes in reusing processes.

In conclusion, the bipolymer-Pd complex possesses remarkably higher hydrogenation activity and stability than the single polymer-Pd complexes. In addition, the catalytic activity was obviously influenced by the interaction between the bipolymer-Pd complex and the substrate and the steric effect of substrates. It is also exhibited that the bipolymer-Pd complex have good catalytic selectivity. The study on the structure of the bipolymer-Pd complexes and the relationship between the structure and properties will be reported in the successive paper.

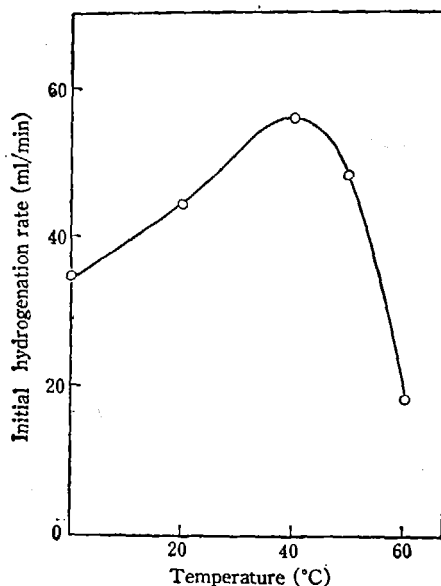


Fig. 5 Relationship between the hydrogenation rate and the temperature by PSSA-Pd-PAA

Other conditions are the same as Fig. 2.

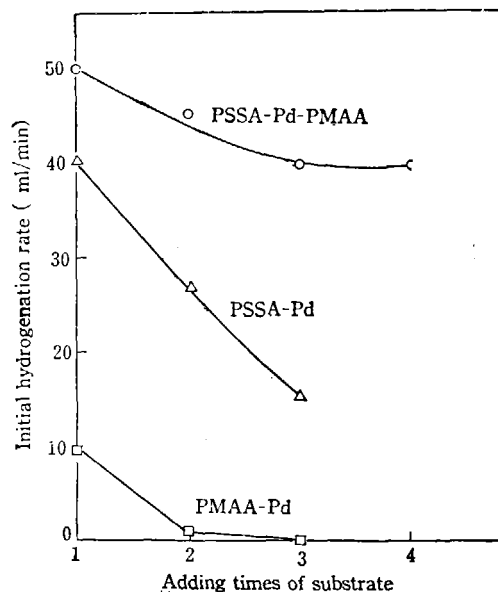


Fig. 6 The stability of bipolymer-Pd and single polymer-Pd complexes.
Pd, 0.025 mg atom; Monomeric unit, 0.1 mmol;
PhNO₂, 0.005 mol; Solvent, methanol; Total reaction
volume, 25 ml; 30°C, 1 atm.

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