

# The Compatibility of a Polymer Catalyst–Substrate–Solvent and its Reaction Rate. I

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## Synopsis

An attempt was made which expressed in a compatibility rule not only the polymer effect but the solvent effect in a given polymeric catalyst system. Here the compatibility refers to interaction energy effects among the polymer backbone, substrate, and solvent, which can be measured by cohesive energy density or the solubility parameter. A polymer catalyst adopted here is poly(diethylaminoethyl acrylate)–palladium ion complex. The experiments showed that the activity of the polymer catalyst had a bell-shaped solubility parameter profile and an optimum solubility parameter value for some substrates, and had an inverse bell-shaped solubility parameter profile and a minimum solubility parameter value for some solvents. Perhaps these results might be utilized to design a polymer catalyst having high activity for a given substrate.

## INTRODUCTION

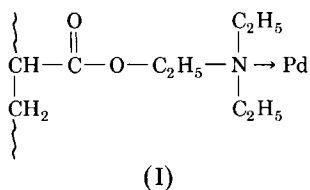
In recent years, many researchers on catalytic hydrogenation of some organic compounds by polymer catalysts have been reported. They include some interrelations of catalyst properties and structures.<sup>1–4</sup> No attempt is made here to describe in detail the quantitative interrelations of structure and properties. In this article, the authors try to mention quantitatively how the microstructural parameter of a polymeric backbone of the polymeric catalyst effects the activity of that catalyst. The experiments revealed that the activity of the polymer catalyst was concerned in the solubility parameter of the polymer backbone and also in substrates and solvents.

It is well known that a polymer catalyst can change some caustic conditions needed in some chemical reactions into general temperature and atmosphere. This should be attributed to macromolecule effects which involve cooperative, electrostatic, clathrate, and feedback effects of polymers, which have been advanced before. The authors think that the macromolecule effects should include interaction energies among the mixing components and could be expressed in solubility parameters of polymer backbone, substrates, and solvents in a catalysis system using a polymeric catalyst.

For a heterogeneous catalytic reaction system, the first step is of absorption of substrate onto the surface of the solid catalyst, and the last step is of desorption of the product from it during the reaction process, according to the catalytic theory. It seems likely that the absorption or desorption in a solid catalytic process is related to the compatibility between the polymer catalyst and the substrate or the solvent. A good compatibility of a polymer catalyst with a substrate can create a higher concentration around the active site of

the catalyst than in the solvent. Because the rate is directly proportional to the concentration, the higher the concentration around the active site of the catalyst is, the higher the reaction rate is. Quite the contrary, the rate is lower. In addition, the reaction rate is also related to the compatibility between the solvents and the substrates. According to solution theory, the compatibility can be measured by solubility parameters of various mixing components.

For this reason, we synthesized a new polymer-metal complex catalyst—poly(diethylaminoethyl acrylate)—palladium ion complex (see I below)—and investigated the interaction energies of various molecules in the catalysis system. The experiments showed that the activities of the polymer catalyst had a bell-shaped solubility parameters profile and an optimum value for some substrates, and also an inverse bell-shaped solubility parameters profile and a minimum value for some solvents. These facts might be utilized in seeking to design a polymer catalyst having high activity for a given substrate:



## EXPERIMENTS

### Preparation of Silica-Supported Poly(diethylaminoethyl Acrylate) (PDEAEA)

A mixture of 20 g of silica and 10 g of diethylaminoethyl acrylate was added to 80 mL of an aqueous solution containing 0.2 g of potassium persulfate. The polymerization of the monomer carried out at 60°C for 2–3 h, resulting in a white solid powder. Then the product was filled and washed with ethanol for four times to extract unreacted monomer. After drying at vacuum, a silica-supported PDEAEA was obtained.

The ratio of the PDEAEA to silica was equal to 0.36:1. (using three-acid decomposition on the silica-supported PDEAEA and weighing analysis).

### Coordination of the PDEAEA with Palladium Ion

A given amount of the silica-supported PDEAEA powder was added into an aqueous solution of palladium chloride in a given concentration. The mixture was heated at 90°C for 10 h, resulting in a black powder. Then the black powder was thoroughly washed with distilled water and dried, obtaining a PDEAEA–Pd complex.

Note that when the PDEAEA was treated with palladium chloride at 90°C for a longer time, its color changed to black, indicating the palladium ion coordination. The coordination of the nitrogen atom on the PDEAEA with the palladium ion was also revealed by infrared spectrum.

The content of palladium ion coordinated to the PDEAEA was measured by means of atom absorption spectrum. The ratio of nitrogen to palladium was equal to 3.7:1.

### Measurement of Activity of the PDEAEA-Pd Catalyst

The catalysis rate of the PDEAEA-Pd catalyst for hydrogenation of substrates was indicated by the original rate of uptake hydrogen (mL/min). The catalysis system is shown in detail in the notation of star in Tables I and II. The catalysis reaction proceeded under constant stirring.

## RESULTS AND DISCUSSION

### Interaction Energies and Compatibilities among Mixing Components

At present, the cohesive energy density is used as the underlying points for the discussion of compatibility among mixing components.

The cohesive energy density (CED) is defined as the following formula:

$$(\text{CED}) = -0.5(n\epsilon Z)/V$$

where  $N$  represents the Avogadro number,  $\epsilon$  represents interaction energy per bond, and  $V$  represents volume.

The solubility parameter is defined as the square root of the cohesive energy density:

$$\delta = (\text{CED})^{1/2}$$

Interaction energies of molecules are related to each other in the following manner. Mixing solvent 1 and polymer 2 produces two solvent polymer 1-2 bonds for every broken solvent-solvent 1-1 and polymer-polymer 2-2 bond. The change in interaction energy during the mixing process is consequently

$$\Delta\epsilon = \epsilon_{12} - 0.5(\epsilon_{11} + \epsilon_{22})$$

Assuming only dispersion forces, without hydrogen bond and equal molar volume of solvent and polymer units, we have

$$\frac{0.5ZN\Delta\epsilon}{V^m} = -0.5(\delta_1 - \delta_2)^2$$

where  $\Delta\epsilon$  is the change in interaction energy during the mixing process,  $V^m$  is the molar volume,  $Z$  is the neighbor number around a molecule or a polymer unit,  $\delta_1$  is the solubility parameter of solvent, and  $\delta_2$  is the solubility parameter of polymer.

The difference in solubility parameters thus yields a measure of the interaction energies between a solvent and a polymer with respect to mutual interaction between like components. When the difference between the solvent and the polymer solubility parameter is equal to zero, indicating a good compatibility between like components. Hence a good compatibility of a polymer catalyst with a substrate is able to create a good environment, i.e., a higher concentration around the active site of the polymer catalyst than in the solvent, increasing the catalytic reaction rate. The experimental results were illustrative of these cases.

*Compatibilities of Polymer Catalyst with Substrates and Its Activities*

The experiments revealed that the activities of the polymer catalyst had a bell-shaped solubility parameters profile and an optimum solubility parameter value for some substrates (see Table I and Fig. 1). These phenomena are interpreted in terms of compatibility of component species. As mentioned above, the smaller the differences of solubility parameters of polymer back-

TABLE I  
Solubility Parameters of Polymer Backbone-Substrates-Products and Rates of  
Hydrogen Uptake in Catalytic Reactions<sup>a</sup>

Substrate	$\delta$ (cal/cm <sup>3</sup> )	Product	$\delta$ (cal/cm <sup>3</sup> )	$R^*$ (mL/min)
Methyl methacrylate	8.8	Methyl isobutyrate	8.3	7.45
Vinyl acetate	9.0	Ethyl acetate	9.1	11.40
Nitrobenzene	10.0	Aniline	10.3	13.00
Methacrylic acid	11.2	Isobutyric acid	10.3	8.25
Allyl alcohol	11.8	Propanol	11.9	5.10
Acrylonitrile	10.5	Ethyl cyanide	10.9	3.95
Acrylic acid	12.0	Propionic acid	9.9	6.30
Polymer backbone	$\delta^*$ (cal/cm <sup>3</sup> )			
PDEAEA	10.02			

<sup>a</sup> $R^*$  = rate of hydrogen uptake in catalytic reaction;  $\delta^*$  = the solubility parameter of poly(diethylaminoethyl acrylate) is 10.02 (cal/cm<sup>3</sup>) according to the equation  $\delta^* = F/V$ , where  $F$  is mole constant of attraction in repeat unit and  $V$  is mole volume in repeat unit based on the Small's group summation method; \*reaction system: amount of Pd<sup>+</sup>, 0.10 mmol; substrates, 0.05 mol; solvent, acetic acetate; volume of reaction mixture, 25 mL; reaction temperature, 20°C; pressure, 1 atm.

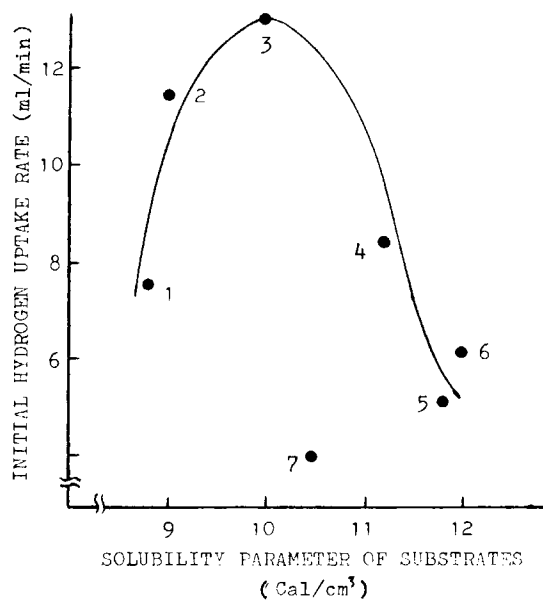


Fig. 1. Relationship between reaction rates and solubility parameters of substrates: (1) methyl methacrylate; (2) vinyl acetate; (3) nitrobenzene; (4) methacrylic acid; (5) allyl alcohol; (6) acrylic acid; (7) acrylonitrile.

bone from substrates are, the higher the concentrations on the surface of the polymer catalyst. Because the activity of the polymer catalyst is determined by concentration of substrate on the surface of the polymer catalyst, the activity of the catalyst increases with decreasing difference of solubility parameter of polymer backbone from substrates. It can be seen from Figure 1, point 3, that the difference between solubility parameters of the polymer backbone and nitrobenzene is smaller than that of all other substrates, namely, the nitrobenzene molecules concentrated on the surface of the polymer catalyst are more than that of other substrates, hydrogenation rate of the nitrobenzene is thus highest (see Figure 1, point 3). On the other hand, an exception is the hydrogen-absorption rate of acrylonitrile which is very low and far departs the curve (see Fig. 1, point 7). This could be thought of catalyst poison, that is, the nitrogen atom on the acrylonitrile is coordinated onto the palladium ion in the polymer catalyst, poisoning the catalyst.

*Compatibilities of Solvent with Substrates and Activities of the Polymer Catalysts*

The experiments indicated that the activities of the polymer catalyst had an inverse bell-shaped solubility parameters profile and a minimum solubility parameter value for solvents (see Table II and Fig. 2). As already stated, the reaction rate of a polymer catalyst in a given system is determined by concentrations on the surface of the catalyst. On the other hand, there is a substrate partition between the surface of polymer catalyst and solvent when various solvents are adopted. This partition depends on compatibilities determined by difference between the solubility parameters of the substrate and the polymer catalyst, and various solvents. If the difference of solubility parameter of substrate from solvent is larger than that from polymer backbone, the concentration of the substrate in the solvent is smaller than that on the surface of the polymer catalyst. Conversely, the concentration of substrate in the solvent is larger than that on the surface of the catalyst. The former will increase the activity of the polymer catalyst, the latter will decrease the activity of the polymer catalyst. From the standpoint of compatibility, it is easy to explain those phenomena above. For example, the difference between the solubility parameters of vinyl acetate and DMF is  $3 \text{ (cal/cm}^3)^{1/2}$ , and polymer backbone is  $0.92 \text{ (cal/cm}^3)^{1/2}$  (see Table I). The concentration of

TABLE II  
Solubility Parameters of Various Solvents and Rates of Hydrogen Uptake in Catalytic Reaction<sup>a</sup>

Solvent	$\delta \text{ (cal/cm}^3)$	Rate of H <sub>2</sub> uptake (mL/min)
Cyclohexane	8.2	14.40
Toluene	8.9	6.80
Benzene	9.2	5.00
Dioxane-1,4	10.0	5.30
Acetophenol	10.6	6.50
DMF + acetophenol*	11.5	8.90
DMF	12.1	12.90

<sup>a</sup>\* = reaction system: amount of Pd<sup>++</sup>, 0.10 mmol; substrate (vinyl acetate), 0.05 mol; volume of reaction mixture, 25 mL; reaction temperature, 20°C; pressure, 1 atm. \*\*DMF:acetophenol = 0.6:1.0.

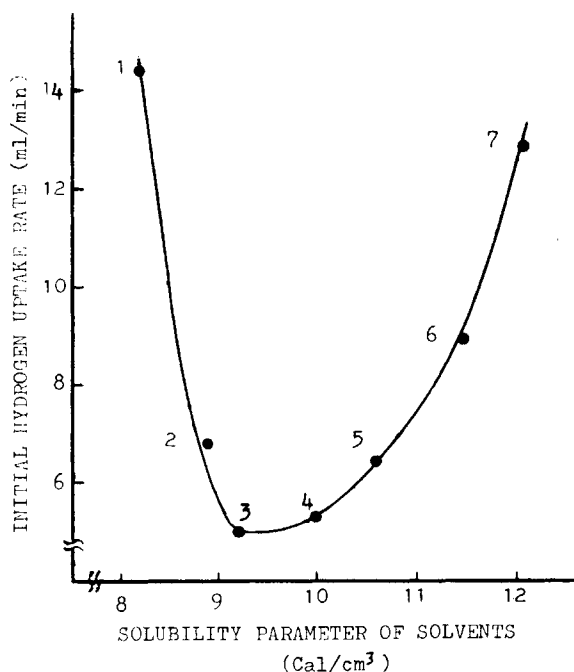


Fig. 2. Relationship between reaction rates and solubility parameters of solvents: (1) cyclohexane; (2) toluene; (3) benzene; (4) dioxane-1; (5) acetophenol; (6) DMF + acetophenol; (7) DMF.

vinyl acetate on the surface of the polymer catalyst is thus higher than in DMF. The polymer catalyst thereby has a high activity (Fig. 2, point 7). On the other hand, the difference between the solubility parameters of vinyl acetate and benzene is almost equal to zero, while that of polymer backbone is  $0.92 (\text{cal}/\text{cm}^3)^{1/2}$ . Thus the concentration of vinyl acetate on the surface of the catalyst is lower than in benzene; therefore the catalyst has a low activity relatively (see Fig. 2, point 3).

### Compatibilities among Components and Design of a Polymer Catalyst

The aim of this article is an attempt to seek to express, in the compatibility rule among mixing components, not only the polymer effect but also the solvent effect in a given polymeric catalysis system. The compatibility refers to interaction energy density measured by solubility parameter. Because the solubility parameter is only good for dispersion forces occurring in matter, all the components in this catalysis system should be confined by matter species held together by dispersion forces. Based on this, all nonpolar are the polymeric catalyst substrates and solvents selected in the experiments. Those components here were arbitrarily extended to weekly polar species without an ability forming hydrogen bond with polymer backbone. It seems successful more or less that the compatibility rule was utilized for explaining the polymer effect in this catalytic system using the polymeric catalyst. As a result, it is hoped that the compatibility rule in this polymeric catalyst system

perhaps likely induces one to seek designing a polymeric catalyst having a high activity for a given substrate. There were two polymer effects which would be advanced to design a polymeric catalyst except for the hydrogen bond. First, the difference of solubility parameters between a polymer backbone and a given substrate needed to be reduced to minimum and referred to as zero. Second, the difference of solubility parameters between the substrates and a selected solvent required increasing to maximum as much as possible except that the substrate and the solvent are incompatible with each other.

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