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## Polymerization of Vinylacetylene with Transition Metal Catalysts- An Approach to Synthesis of Conjugated Polymer

S. M. Abdul Karim\*

*Abstract :* Vinylacetylene (VA) was successfully polymerized by Rh-based catalysts resulting in a moderate yield (~53%). The obtained polymers are almost black in color which indicates extended conjugation of the main chain. The resulting polymers were partly soluble in chloroform, THF, mostly soluble in DMF, and insoluble in hexane, ethanol etc.  $Et_3N$  was used as a co-catalyst. Toluene was effective as a solvent while polar solvent was ineffective. IR spectra of the polymer showed no peak at around  $2200\text{ cm}^{-1}$  which is ascribed to ethynyl group, indicated that ethynyl group was polymerized efficiently to give rise to conjugated polymer.

**Keywords :** Conjugated polymer, Vinylacetylene, Transition metal catalyst

### Introduction

Conjugated polymers have drawn great attention in ongoing polymer research because of their interesting optical, electrical, and magnetic properties.<sup>1</sup> Tremendous advances have been made in these past decades in the discovery of new conjugated polymers, in the improvement of their preparative methods, and in the tailoring of their properties. These developments have undoubtedly originated from the finding of conductivity as high as that of copper metal in polyacetylene in 1970s, which has led to the creation of a variety of conjugated polymers including poly (thiophene)s, poly (pyrrole)s, poly (*p*-phenylene)s, poly (aniline)s, and so on. Notwithstanding the greatest contribution of polyacetylene to this new field, its practical application as a functional material is quite limited because of lacking processability, solubility, and stability.<sup>2,3</sup> Incorporation of appropriate substituents enables the production of polymers with improved solubility and processability (**Chart 1**).<sup>4,5</sup> Simultaneously, however, the conjugation of the main chain is drastically reduced because the repulsion between the pendant groups causes a twist of the main chain. Thus, most of the polymers from substituted acetylenes are colorless or only slight-

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ly colored and show quite low unpaired-electron densities. However, it has been found from the recent studies that acetylene polymers possessing considerably wide conjugation can be obtained from monosubstituted acetylene by appropriate selection of the substituents.<sup>6-9</sup>

Vinylacetylene (VA) is a well known reactive organic compound which has two functional groups: one is vinyl group and another is ethynyl group. Although it has been often used in organic synthesis for making new compounds, its use in polymerization is rare. Considering the ethynyl group as a reacting unit in the polymerization reaction, and if it is possible to obtain acetylene polymer by applying appropriate metal catalyst, it is expected that the resultant polymer would certainly be an interesting substituted acetylene polymer since the main chain and the substituent would possess double bonds which is nearly similar to the construction of widely conjugated polyacetylene. Therefore, Poly(VA) are expected to provide widely conjugated polymer. Focusing on this matter, the polymerization of VA has been explored. In this article, the polymerization of VA, the structure and properties of the obtained polymers has been reported.

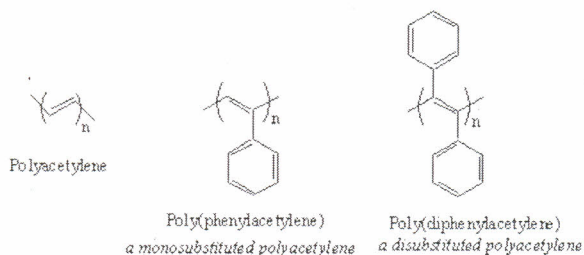


Chart 1 Polyacetylene and some of its derivatives

## Experimental

### General

All of the polymerization runs were carried out in standard laboratory glassware. Monomer, vinylacetylene (VA), was offered by Denki Kagaku Kogyo Kabushikikaisha as 0.2 and 0.5 M solution in toluene and DMF.  $[\text{Rh}(\text{nbd})\text{Cl}]_2$  was purchased from Aldrich and  $[\text{Rh}(\text{cod})\text{Cl}]_2$  was prepared according to the standard method. Solvents were used as purchased. All the reactions were carried out under  $\text{N}_2$ . IR, UV-visible and NMR spectra were recorded on a Shimadzu FTIR-8100 spectrophotometer, a Shimadzu UV-2200 spectrophotometer, and a JEOL EX-400 spectrometer, respectively.



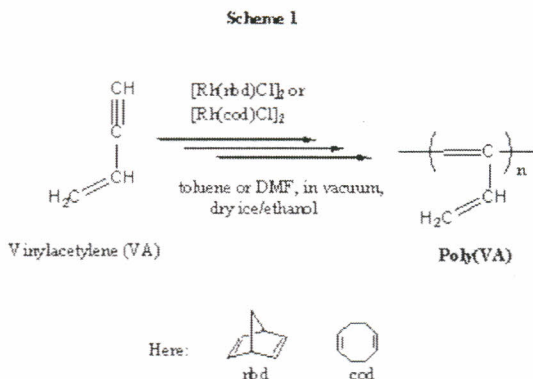
## Polymerization

A typical procedure: Polymerizations were performed in a Schlenk tube equipped with a three way stopcock under a nitrogen atmosphere. Schlenk tube charged with a solution of monomer, VA, was kept in dry-ice/ethanol (-76°C) and then catalyst was added into the solution. Cocatalyst, Et<sub>3</sub>N, was added few minutes after stirring the solution. The concentrations of the monomer, catalysts and cocatalyst are denoted in **Table 1**. Temperature was raised slowly to room temperature and the solution was stirred for 24 h at ambient temperature. After the reaction is over the resulting solution was dried under reduced pressure to obtain the polymer solid. The yields of the polymers were calculated by gravimetric method.

## Result and Discussion

For the polymerization of substituted acetylenes, proper selection of the catalysts is essential.<sup>4</sup> Studies showed that for the polymerization of monosubstituted

acetylenes, Rh (Rhodium), W (Tungsten) and Mo (Molybdenum) based catalysts are effective. Among these catalysts, Rh-based ones possess enough stability and high tolerance towards functional groups. For instance, acetylene monomer having imino group (-C=N-) provides high polymer when Rh is used as a catalyst whereas W and Mo based catalysts are readily deactivated by this functional group to result in little or no polymer. Since VA is a highly reactive monomer, we chose especially Rh-based catalysts for the present polymerization considering the above findings. Polymerization reaction is shown in **Scheme 1**. It should be noted that in case of Rh-based catalysts, polymerization proceeds via insertion mechanism while polymerization by W and Mo catalysts progress via metathesis mechanism.



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The results of the polymerization are shown in Table 1. The progress of the polymerization was monitored by observing color change of the solution. The mixture was turned into red just after adding monomer solution in the catalyst-cocatalyst mixture, and gradually became black in color. It was found that the reaction was proceeded in a very slow fashion without cocatalyst. The polymer was obtained by vacuum evaporation of the solution. Both [Rh(nbd)Cl]<sub>2</sub> and [Rh(cod)Cl]<sub>2</sub> gave dark brown to black polymer.

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**Table 1. Polymerization Results of VA with Rh Catalysts**

Entry	[M] <sub>0</sub> (M)	Catalyst	[Cat] (mM)	[Cocat] <sup>a)</sup> (mM)	Yield <sup>b)</sup> (%)
1	0.2 in toluene	[Rh(nbd)Cl] <sub>2</sub>	3	18	53
2	0.5 in toluene	[Rh(nbd)Cl] <sub>2</sub>	3	18	19
3	0.2 in toluene	[Rh(cod)Cl] <sub>2</sub>	3	18	36
4	0.5 in DMF	[Rh(nbd)Cl] <sub>2</sub>	3	18	33.7
5	0.5 in DMF	[Rh(cod)Cl] <sub>2</sub>	3	18	23.2

a) Cocatalyst = Et<sub>3</sub>N; b) Calculated by gravimetric method

vacuum evaporation of the solution. Both [Rh(nbd)Cl]<sub>2</sub> and [Rh(cod)Cl]<sub>2</sub> gave dark brown to black polymer.

[Rh(nbd)Cl]<sub>2</sub> provided relatively high yield (53%) than that of [Rh(cod)Cl]<sub>2</sub> (36%). It may be attributed to the difference of dissociation between Rh-(nbd) bond and Rh-(cod) bond. It has been found that norbornadiene (nbd) has loose bonds than cyclooctadiene (cod) with Rh which makes Rh catalyst to react easily in case of [Rh(nbd)Cl]<sub>2</sub>. The overall yield is fair to low in any case, it is probably due to containing stabilizer, TBC (4-*t*-butyl catechol), in the monomer solution which suppressed and/or inhibited the progress of the reaction. The effect of the monomer concentration was also observed. Low concentration of the monomer irrespective of the solvents used provided comparatively high yields. Solvents effect was also examined. Polar solvents such as DMF seem not effective for the polymerization. It may be interpreted in the way that polar solvents affect in the bond dissociation of the catalyst in the solution which greatly influence in the polymerization reactions. The obtained polymers were almost black in color which indicates the extended conjugation of the main chain. The polymers were partly soluble in chloroform, THF, mostly soluble in DMF and insoluble in Hexane, ethanol etc.

The polymers were attempted to characterize by IR and NMR spectroscopy. In IR spectra, complicated peaks were observed due to containing catalyst with the resulting polymer which gave additional peaks along with that of polymer. It is, however, new peaks characteristics to the acetylene polymers were observed which

indicates that the monomer was polymerized. Moreover, the peak of ethynyl group ( $-C\equiv C-$ ) which appears around  $2100\text{ cm}^{-1}$  is absent in these polymers spectra. These results suggest that ethynyl (acetylene) group was polymerized in these reactions.  $^1\text{H-NMR}$  data gave no clear view to recognize the polymer. UV-visible spectra showed cutoff at around  $700\text{ nm}$  with no distinct absorption maxima. No absorption was observed in this region in the UV-visible spectrum of vinylacetylene monomer. Therefore, polymer shows a red shifted absorption which can be attributed to the electronic transitions of the main-chain chromophores. Thus the observed absorption results from the conjugation along the back bone of the polymer. UV-visible spectra was unchanged even after bubbling by air for about 1 hour which indicates that the polymers are stable in the air.

In conclusion, VA can be polymerized by Rh-based catalyst successfully. The polymers are extensively conjugated which is very difficult to obtain from mono-substituted acetylenes. These polymers are expected to be a unique optoelectronics materials. More studies are necessary to clarify the structure.

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