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EFFECTS OF SUBSTITUENT GROUPS AND SUBSTITUTED BENZENES ON THE POLYMERIZATION OF PHENYLACETYLENES INITIATED BY DI-μ-PENTAFLUOROTHIOPHENOLATE BIS(1,5-CYCLOOCTADIENE) RHODIUM(I)

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Abstract—In order to study the mechanism of polymerization of phenylacetylene initiated by rhodium catalysts, the polymerization of phenylacetylene was carried out in the presence of various substituted benzenes. It was found that the benzenes with electron donor substituents had little effect on the polymerization, while those with carbonyl and nitrile groups had negative effects. However, p-ethynylmethylbenzoate polymerized more rapidly than p-methoxyphenylacetylene and phenylacetylene, suggesting that the acidity of acetylenic hydrogen is most important for the polymerization. A proton transfer mechanism is proposed as a mechanism of the polymerization.

INTRODUCTION

The polymerization of phenylacetylene has been studied by many workers in the last few decades. Kern has studied catalytic and thermal polymerization of phenylacetylene and obtained low molecular weight polymers [1]. Simionescu *et al.* [2] have reported an extensive study of characterization of products obtained by anionic polymerization of phenylacetylene. Tungsten and molybdenum catalyst systems have been studied by Katz and coworkers [3]. Masuda *et al.* [4] have obtained high molecular weight polymers of various phenylacetylenes using molybdenum-based catalysts, and they proposed a living metathesis polymerization mechanism. The organometallic compounds of metals of groups 8, 9 and 10 are also known to catalyze the polymerization of acetylenes. Sen and Lai [5] have used palladium-based catalyst, and Furlani *et al.* have reported the polymerization of phenylacetylene with nickel [6] and platinum [7] catalysts. Various rhodium compounds have been reported in the literature as effective catalysts for the polymerization of acetylenes. Furlani *et al.* [8] have polymerized phenylacetylene using rhodium catalysts such as $[Rh(COD)Cl]_2$, $[Rh(COD)bipy]PF_6$ and $[Rh(NBD)bipy]PF_6$. Tabata *et al.* [9] have obtained polyphenylacetylene with very high molecular weights using a $[Rh(NBD)Cl]_2$-triethylamine catalytic system, and they suggested that a living polymerization is taking place. The rhodium compounds appear to be very effective for the polymerization of phenylacetylene. The polymers have high molecular weights and a stereoregularity. However, the mechanism has not been totally clarified, although it has been discussed in the above references. The present authors have recently reported the polymerization of phenylacetylene using di-m-pentafluorothiophenolate bis(1,5-cyclooctadiene)rhodium(I) and its analogues, and suggested a proton transfer mechanism for the polymerization [10]. In this work, various substituted benzenes were added to the polymerization systems of phenylacetylene in order to study the effects of functional groups on the polymerization. The polymerization of some p-substituted phenylacetylenes was carried out, and the polymerization mechanism is discussed in this report.

EXPERIMENTAL

Materials

Phenylacetylene (PA) and p-ethynyltoluene (ET) were supplied by Aldrich, and they were distilled over calcium hydride before use. p-Methoxyphenylacetylene (MA) was synthesized from p-methoxycinnamic acid by the method reported previously [11] as shown in Scheme 1.

Colourless crystals melting at 29°C and boiling at 90–95°C/10 mmHg were obtained. p-Ethynylmethylbenzoate (EB) was prepared by the reactions as shown in Scheme 2.

Colourless crystals melting at 90–92°C were obtained. These acetylenes were confirmed to be pure by elemental analysis, IR and NMR spectroscopy, and thin layer chromatography. Tetrahydrofuran (THF) used as solvent, was distilled over calcium hydride. All of the additives used for the polymerization of PA were of reagent grade supplied by Aldrich, and they were used as received. The rhodium catalyst was prepared by the method reported previously [10].

Polymerization

The polymerization of PA in the presence of added substituted benzenes was carried out as follows. To a 100 ml

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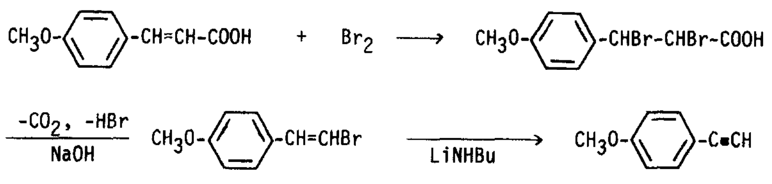


Scheme 1

3-necked flask were added 17 ml of dry THF and 2.61×10^{-5} mol of the catalyst under nitrogen and the system was stirred for several minutes. Then a mixture of 2.52×10^{-2} mol of PA and 1 ml of additive were added under nitrogen, and the system was stirred at room temperature for 4 hr, during which 2 ml of the solution was taken out at time intervals and was poured into 200 ml of methanol to precipitate poly-PA. The polymerization of p-substituted PAs was carried out similarly to the above, but without additives.

Characterization

The molecular weights of the polymers were determined in THF at room temperature by GPC using a Waters ALC/GPC-501 equipped with a Waters 410 differential refractometer and three columns of Ultrastyragel (lineal, 500A and 100A).

RESULTS AND DISCUSSION

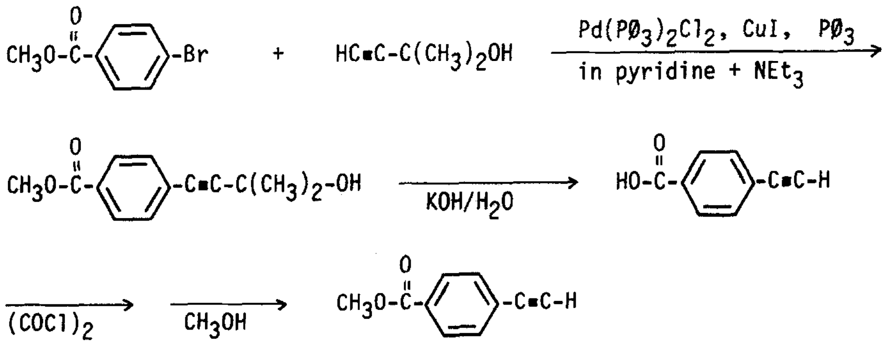
The polymerization of PA was carried out in different solvents and it was found that THF was a good solvent for the polymerization, as shown in Table 1. The dielectric constant of the solvent might appear to be important, from the data in Table 1. However, a comparison of the case of dichloroethane with that of THF, or with that of dioxane, does not suggest a significant correlation between the dielectric constant of the solvent and the polymerization. It has been reported that triethylamine ($D = 2.44$) accelerates the polymerization of PA giving extremely high molecular weight polymers [9]. It may be concluded that the basicity of the solvents is more important than the dielectric constant.

In order to discuss the effects of substituent groups of PA on the polymerization, the polymerization of PA in the presence of various substituted benzenes was carried out, and the results are shown in Table 2. It can be seen that the carbonyl-substituted benzenes had a negative effect on the polymerization, benzaldehyde inhibiting totally the polymerization. Others having electron donor groups and nitrobenzene did not show any appreciable effect, the effect being more or less the same as that of benzene. The fact that the polymerization is not inhibited by nitrobenzene, suggests that the polymerization is not of anionic character. In order to discuss the mechanism of the polymerization of PA with this catalyst, it should be mentioned that the catalyst is stable in air and against humidity, and does not decompose easily like other polymerization catalysts, such as the Ziegler–Natta type or the metathesis type, such as WCL_6. It was found that the catalyst polymerizes only PAs, and not alkynes, olefins and internal acetylenes such as 1-methyl-2-phenylacetylene. The copolymerization of PA with styrene was attempted, and only homopolymer of PA was obtained, styrene acting only as a solvent. The polymerization of PA took place in the presence of methanol and in wet THF without noticeable retardation, which means that the propagating species is not an active carbanion or carbocation. It was previously confirmed by an NMR study [11] that no ligand decoordinates from the Rh metal during the polymerization of PA. NMR spectra of the catalyst and of an equimolecular mixture of the catalyst with benzaldehyde were taken, in order to see if there was any interaction of benzaldehyde, the polymerization inhibitor, with the Rh metal. The peaks of coordinated cyclooctadiene, 4.56 ppm (=C–H) and 2.1 ppm (CH_2), did not change

Table 1. Effect of solvent on the polymerization of PA*

Solvent	Dielectric constant (D)	Yield (%)	$M_n \times 10^{-4}$
1,2-Dichloroethane	10.37	19.4	0.15
1,4-Dioxane	2.21	19.7	0.20
Benzene	2.27	5.4	0.13
Tetrahydrofuran	7.39	50.2	1.13

*Polymerization at room temperature under N_2 for 5 hr. $[M] = 2.73 \times 10^{-2}$ mol. $[C] = 1.22 \times 10^{-5}$ mol. [Solvent] = 3 ml.



Scheme 2

Table 2. Effect of additives on the polymerization of PA

R– of R–∅	–H		$-NH_2$		$[N(CH_3)_2$		EtO–		CH_3OCO–		–CHO		–CN		$-NO_2$	
Polymerization time (min)	Yield (%)	M_n (10^{-4})	Yield (%)	M_n (10^{-4})	Yield (%)	M_n (10^{-4})	Yield (%)	M_n (10^{-4})	Yield (%)	M_n (10^{-4})	Yield (%)	M_n (10^{-4})	Yield (%)	M_n (10^{-4})	Yield (%)	M_n (10^{-4})
10	7.1	1.3	3.6	1.0	9.3	0.6	8.1	2.3	—	—	0	—	2.0	—	5.5	2.9
20	9.0	2.7	9.8	1.7	11.0	1.0	9.1	2.6	1.7	0.3	0	—	2.6	—	7.4	2.9
30	12.4	2.9	21.2	2.8	15.1	1.7	14.0	3.2	2.3	0.3	0	—	2.6	—	9.1	3.0
60	23.3	2.2	28.5	3.6	24.4	1.7	25.5	3.3	4.2	1.0	0	—	2.6	—	16.1	1.9
120	45.5	2.3	43.1	4.8	37.6	2.0	41.4	4.5	7.2	1.0	0	—	4.0	0.7	42.5	2.3
240	90.0	2.5	100	4.5	69.5	2.4	100	1.3	20.0	1.0	0	—	14.8	1.1	89.6	1.0

Experimental conditions: see Experimental section.

their positions on the addition of benzaldehyde, indicating that benzaldehyde does not coordinate to the Rh metal.

The Rh metal of this catalyst (planar) can coordinate one more ligand providing its 4-d orbital, which is used to coordinate the monomer, forming a metastable square pyramidal transition state. If a basic solvent or additive occupies this coordination site, the coordination of the monomer is blocked and the polymerization must be retarded or inhibited. Furlani *et al.* [8] have proposed a mechanism in which the Rh metal decoordinates one ligand of cyclooctadiene to accommodate the monomer for their catalyst systems, but no experimental evidence was provided. It should be borne in mind that the Rh metal is a very soft acid and amines and carbonyl oxygen are hard bases.

The Rh metal of this work does not have an anionic species to add and initiate the polymerization of PA, as in the case of ethyl anion of the $TiCl_4/AlEt_3$ system, and therefore it is unlikely that Rh metal forms a positive metal centre like in the case of Ziegler–Natta and anionic polymerizations.

Considering the above-mentioned results and discussions, it can be said that the acidity of the terminal hydrogen of the monomer is of vital importance for the polymerization to take place. The reason why 1-alkynes and styrene do not polymerize with the catalyst is because their terminal hydrogens are not acidic enough to be transferred.

Table 3. Polymerization of p-substituted phenylacetylenes

R– of R–∅–C≡CH	CH_3OCO–		CH_3–		CH_3O–	
Polymerization time (min)	Yield (%)	M_n (10^{-4})	Yield (%)	M_n (10^{-4})	Yield (%)	M_n (10^{-4})
10	3.2	3.8	0	—	0	—
20	4.9	3.8	0	—	0	—
30	6.8	3.4	3.2	—	0	—
60	11.0	5.9	7.2	1.0	0	—
120	20.2	5.4	18.0	1.6	4.2	3.1
240	39.1	6.3	18.0	3.0	12.3	3.3

Polymerization conditions: same as in Table 2, but without additives.

Table 3 shows the results of the polymerization of p-substituted PAs. It can be seen clearly that the electrondonor-substituted PAs have poorer polymerizability than the electron acceptor-substituted one, in spite of the results shown in Table 2. These results also indicate that no interaction exists between the catalyst and the substituent groups, and the acidity of the acetylenic hydrogen is most important. From the

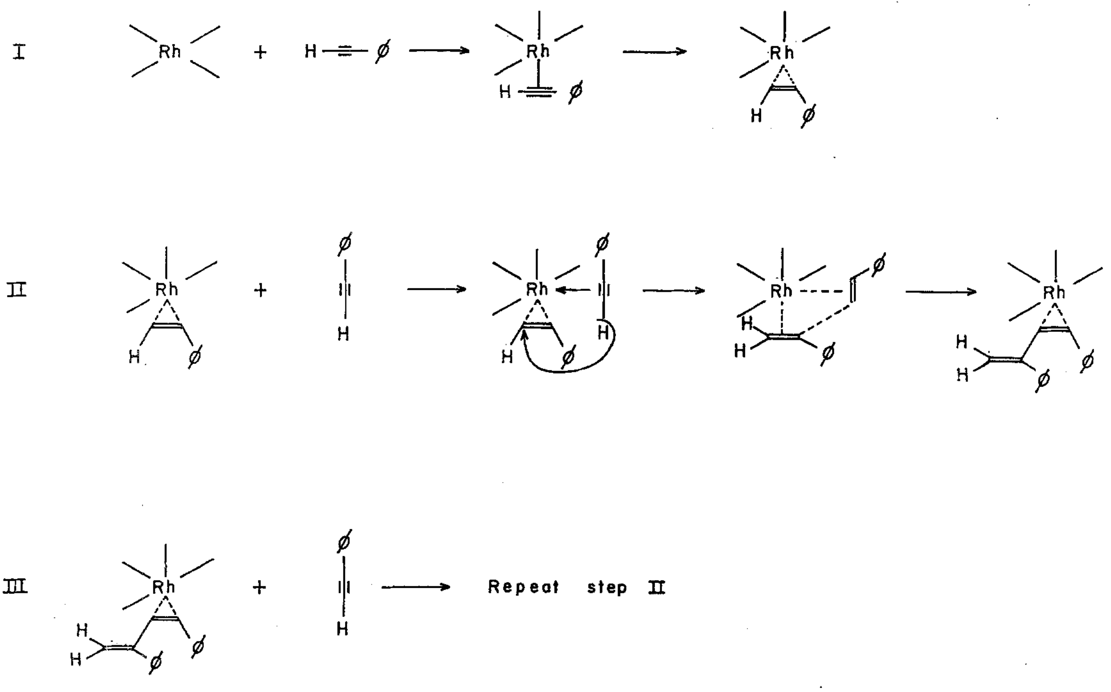


Fig. 1. The proton-transfer mechanism for the polymerization.

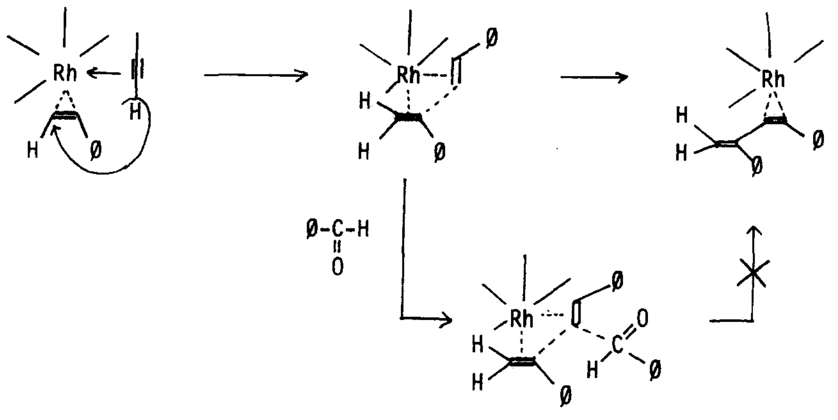


Fig. 2. A probable mechanism of inhibition by benzaldehyde.

results obtained in this work, the following mechanism is proposed for the polymerization of PA with this Rh catalyst, as shown in Fig. 1.

The retarding effect of the aldehyde and ester groups is thought to be due to the interaction of the carbonyl groups with the negative centre of propagating PA in the transition state, thus preventing the propagation, as shown in Fig. 2. Since aldehydes are most susceptible to carbanion attack, this total inhibition by benzaldehyde can be readily understood.

The rapid polymerization of PA in triethylamine (TEA) using $[Rh(NBD)Cl]_2$ by Tabata *et al.* [9], can be understood by this mechanism, TEA facilitating the transfer of proton, although they explained their results by the dimer-monomer dissociation of catalyst caused by TEA, the monomeric form being more active. In

$$\underset{\text{Dimeric form}}{[Rh(NBD)Cl]_2} + TEA \rightarrow \underset{\text{Monomeric form}}{[Rh(NBD)Cl\text{-}TEA]}$$

this case, the Cl may be replaced by TEA, but in the case of this work, such dissociation can be ignored, because Rh–S linkage (soft metal–soft ligand) is more stable than Rh–Cl or Rh–TEA (soft metal–hard ligand).

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