

Copolymerization of phenylacetylene with various acetylenes by W- and Mo-based catalysts*

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In the copolymerization of phenylacetylene with various acetylenes catalysed by $WCl_6 \cdot Ph_4Sn$, the relative reactivity of monomer decreased with increasing steric effect of monomer, e.g. $HC \equiv Cn-Bu$, $HC \equiv Cn-Hex > HC \equiv CPh$, $HC \equiv Cs-Bu > HC \equiv Ct-Bu$, $MeC \equiv CPh$, $ClC \equiv CPh$. While 1-chloro-2-phenylacetylene (a disubstituted acetylene) showed high reactivity in the homopolymerization by Mo-based catalysts, the reactivity was remarkably depressed in the presence of phenylacetylene as comonomer. Based on these results, the relative reactivity of the acetylenic monomers in copolymerization was explained in terms of competitive coordination of monomers to the propagating end.

Keywords Coordination polymerization; copolymerization; monomer reactivity ratios; transition-metal catalysts; phenylacetylene; substituted acetylenes

INTRODUCTION

Substituted acetylenes such as phenylacetylene can be polymerized by W- and Mo-based catalysts². The propagation reaction is inferred to proceed via metal carbenes^{3,4}. It is, however, not known what factors govern the reactivity in the metal-carbene-mediated propagation.

In general, the relative reactivity of a monomer in the propagation reaction can be evaluated from the monomer reactivity ratios (r_1 and r_2) in copolymerization. If the relative reactivities of various substituted acetylenes are obtained, they will provide knowledge about the steric, resonance and polar effects on reactivity, and consequently about the propagation mechanism.

There have been few studies on the copolymerization between substituted acetylenes. We have obtained⁵ a small negative reaction constant ($\rho^+ - 0.47$) from the Hammett relationship in the copolymerization of phenylacetylene with *para*-substituted phenylacetylenes catalysed by WCl_6 . This result supported not a cationic but a coordination polymerization mechanism.

This paper deals with the copolymerization of phenylacetylene with various types of acetylenes by W- and Mo-based catalysts. It has been revealed that the relative reactivity of monomer in copolymerization is governed mainly by the steric factor, indicating that the monomer-coordination stage in propagation plays an important role.

EXPERIMENTAL

Phenylacetylene was prepared by the bromination of styrene and the subsequent dehydrobromination⁶, 1-chloro-2-phenylacetylene was offered by Sanyo Chemical

Industries Ltd, Japan, and other monomers were purchased from Farchan Labs, USA. All the monomers were distilled before use. Transition-metal and organometallic compounds (Alfa Ventron) were usually employed without further purification.

WCl_6 and $MoCl_5$ were mixed with organotins in solution at an equimolar ratio, and the mixtures were aged at 30°C for 15 min before use ($WCl_6 \cdot Ph_4Sn$, $MoCl_5 \cdot n-Bu_4Sn$). A $Mo(CO)_6$ -based catalyst [$Mo(CO)_6-CCl_4-hv$] was prepared as described elsewhere⁷.

Polymerization was usually carried out in toluene at 30°C: $[M]_{0, total} = 1.0$ M, $[Cat] = 5-30$ mM. The polymerization by $Mo(CO)_6-CCl_4-hv$ was performed in carbon tetrachloride at 60°C. The consumption (conversion) of each monomer was determined by measuring the residual monomer concentration by gas chromatography.

Monomer reactivity ratios along with their mean square errors were calculated by the method of Ezziev *et al.*⁸ from data on feed composition and relative consumption of each monomer. Copolymer composition curves (Figures 1-3) were drawn on the basis of the monomer reactivity ratios rather than directly from the plots.

Molecular weights of the copolymerization products were several thousand to about ten thousand. It is probable for the following reasons that mixtures not of homopolymers but copolymers have been formed in the present copolymerizations: (i) the product $r_1 \times r_2$ is usually not much larger than unity; (ii) the molecular weight distributions were unimodal, and further lower and higher molecular weight fractions had the same monomer compositions; (iii) the copolymerization products possessed colours different from those of mixtures of the corresponding homopolymers.

* Part 15 of 'Polymerization of Phenylacetylenes'. For part 14 see ref. 1

RESULTS

Copolymerization catalysed by $WCl_6 \cdot Ph_4Sn$

A 1:1 mixture of WCl_6 with Ph_4Sn ($WCl_6 \cdot Ph_4Sn$) is one of the most active catalysts for the polymerization of phenylacetylene⁹ and various aliphatic acetylenes¹⁰. Since reaction rate and polymer molecular weight often decreased in copolymerization as compared with those in the corresponding homopolymerizations, this highly active catalyst was employed. Toluene was used as copolymerization solvent, because it dissolved well both the catalyst and the polymeric product to effect rapid copolymerization.

Figure 1 shows composition curves for the copolymerizations of phenylacetylene with 1-hexyne, *s*-butylacetylene and *t*-butylacetylene. These three monoalkylacetylenes possess the same molecular formula C_6H_{10} but substituents for which different steric effects are expected. The shapes of the composition curves suggest that random copolymerizations are taking place. From another point of view, this means that the relative reactivities of a pair of monomers do not depend upon whether the propagating end involves phenylacetylene or one of the monoalkylacetylenes.

The relative reactivities of these monomers lie in the following order: 1-hexyne > *s*-butylacetylene \approx phenylacetylene > *t*-butylacetylene. This result leads to the following conclusions: (i) with increasing steric effect in the order of *n*-butyl, *s*-butyl and *t*-butyl, the relative reactivity of monomer clearly decreases, thus indicating the importance of the steric factor; (ii) since the phenyl and *s*-butyl groups should exert similar steric effects, and in fact phenylacetylene and *s*-butylacetylene show similar reactivities, so the resonance effect of the phenyl group hardly contributes to the relative reactivity of phenylacetylene.

Composition curves for the copolymerizations of phenylacetylene with four kinds of octynes are shown in Figure 2. The curve for 1-octyne indicates that, similarly to 1-hexyne, this monomer is randomly copolymerized with phenylacetylene and more reactive than phenylacetylene. On the other hand, the curves for 2-, 3- and 4-octynes (dialkylacetylenes) are very similar to one another but different from that for 1-octyne. The shapes of the curves suggest the copolymerization to be somewhat

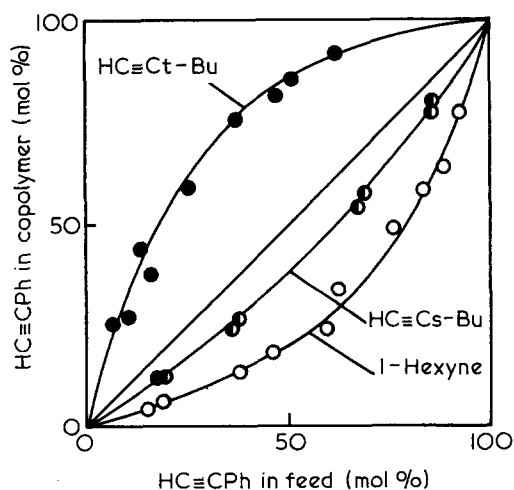


Figure 1 Composition curves for the copolymerizations of phenylacetylene with monoalkylacetylenes by $WCl_6 \cdot Ph_4Sn$ in toluene at 30°C

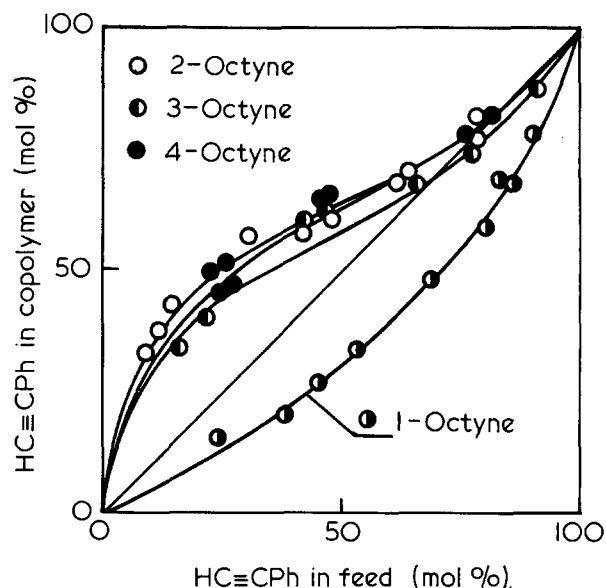


Figure 2 Composition curves for the copolymerizations of phenylacetylene with octynes by $WCl_6 \cdot Ph_4Sn$ in toluene at 30°C

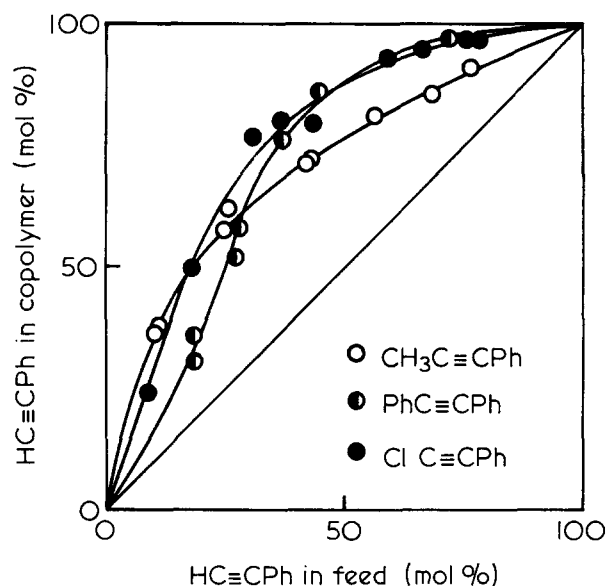


Figure 3 Composition curves for the copolymerizations of phenylacetylene with its derivatives by $WCl_6 \cdot Ph_4Sn$ in toluene at 30°C

alternating. This might be due to the fact that these octynes are somewhat reluctant to undergo homopropagation because of steric hindrance. When the phenylacetylene content of the feed is high, the curves approach the diagonal that passes through the origin. This indicates that the reactivities of these octynes towards the phenylacetylene propagating end are similar to that of phenylacetylene.

Copolymerizations of phenylacetylene with 1-phenyl-1-propyne, diphenylacetylene and 1-chloro-2-phenylacetylene gave the composition curves shown in Figure 3. Electron-donating, resonance and electron-withdrawing effects are anticipated for the methyl, phenyl and chlorine groups, respectively. Nevertheless, the curves show that these phenylacetylene derivatives are all less reactive than phenylacetylene itself. The low reactivity of these monomers can be attributed to the steric effect of the monomers.

The monomer reactivity ratios for the copolymerizations of phenylacetylene (M_1) with various acetylenes are shown in Table 1. The reciprocal of r_1 represents the relative reactivity of a comonomer to phenylacetylene towards the phenylacetylene propagating end. While discussion on small differences in $1/r_1$ is insignificant, monomers can be classified into three main groups according to $1/r_1$: (i) $1/r_1 > 1$, hardly sterically hindered acetylenes ($\text{HC}\equiv\text{Cn-Bu}$, $\text{HC}\equiv\text{Cn-Hex}$); (ii) $1/r_1 \approx 1$, somewhat sterically hindered acetylenes ($\text{HC}\equiv\text{Cs-Bu}$, $\text{MeC}\equiv\text{Cn-Pent}$, etc.); (iii) $1/r_1 < 1$, fairly sterically hindered acetylenes ($\text{HC}\equiv\text{Ct-Bu}$, $\text{MeC}\equiv\text{CPh}$, etc.). Thus the relative reactivity of monomer is successfully correlated with the steric effect of monomer, that is, the bulkiness and number of substituent.

Homo- and copolymerizations by Mo-based catalysts

W-based catalysts polymerize phenylacetylene in high yield², but fail to polymerize 1-chloro-2-phenylacetylene^{1,7}. On the other hand, Mo-based catalysts are not very effective for phenylacetylene, while they polymerize 1-chloro-2-phenylacetylene in high yield.

Examples of such Mo catalysts are as follows: (i) 1:1 mixture of MoCl_5 with tetra-*n*-butyltin¹ ($\text{MoCl}_5 \cdot n\text{-Bu}_4\text{Sn}$); (ii) a catalyst obtained by u.v. irradiation of $\text{Mo}(\text{CO})_6$ in carbon tetrachloride solution⁷ [$\text{Mo}(\text{CO})_6\text{-CCl}_4\text{-}h\nu$]. If the relative reactivity of 1-chloro-2-phenylacetylene to phenylacetylene in copolymerization is examined using these Mo catalysts, the result will help to understand the substituent effect in copolymerization.

In homopolymerizations carried out with $\text{MoCl}_5 \cdot n\text{-Bu}_4\text{Sn}$ under the same conditions, 1-chloro-2-phenylacetylene reacted much faster than phenylacetylene (Figure 4a). In contrast to this, 1-chloro-2-phenylacetylene did not react at all in the copolymerization with phenylacetylene (Figure 4b); phenylacetylene reacted in a similar manner as in homopolymerization. An analogous phenomenon was observed with the $\text{Mo}(\text{CO})_6\text{-CCl}_4\text{-}h\nu$ catalyst (see Figure 5). That is, the reactivity of phenylacetylene in the copolymerization with 1-chloro-2-phenylacetylene hardly changed compared with that in homopolymerization, while that of 1-chloro-2-phenylacetylene was remarkably depressed in the presence of phenylacetylene as comonomer.

Table 1 Monomer reactivity ratios for the copolymerizations of phenylacetylene (M_1) with various acetylenes (M_2) by $\text{WCl}_6 \cdot \text{Ph}_4\text{Sn}^a$

M_2	r_1	r_2	$1/r_1$	Relative reactivity
$\text{HC}\equiv\text{Cn-Bu}$	0.28 ± 0.05	4.27 ± 0.27	3.57	high
$\text{HC}\equiv\text{Cn-Hex}$	0.36 ± 0.03	1.91 ± 0.14	2.78	
$\text{HC}\equiv\text{CPh}$	—	—	(1)	medium
$\text{HC}\equiv\text{Cs-Bu}$	0.59 ± 0.05	1.48 ± 0.08	1.69	
$\text{MeC}\equiv\text{Cn-Pent}$	0.83 ± 0.05	0.12 ± 0.01	1.20	
$\text{EtC}\equiv\text{Cn-Bu}$	0.64 ± 0.05	0.17 ± 0.04	1.56	
$n\text{-PrC}\equiv\text{Cn-Pr}$	0.92 ± 0.07	0.11 ± 0.03	1.09	
$\text{HC}\equiv\text{Ct-Bu}$	7.80 ± 1.03	0.38 ± 0.07	0.13	low
$\text{MeC}\equiv\text{CPh}$	2.86 ± 0.15	0.14 ± 0.02	0.35	
$\text{PhC}\equiv\text{CPh}$	15.0 ± 4.20	1.42 ± 0.54	0.07	
$\text{ClC}\equiv\text{CPh}$	9.05 ± 1.64	0.32 ± 0.20	0.11	

^a Copolymerized in toluene at 30°C; $[\text{M}]_{0,\text{total}} = 1.0 \text{ M}$, $[\text{Cat}] = 5\text{--}30 \text{ mM}$

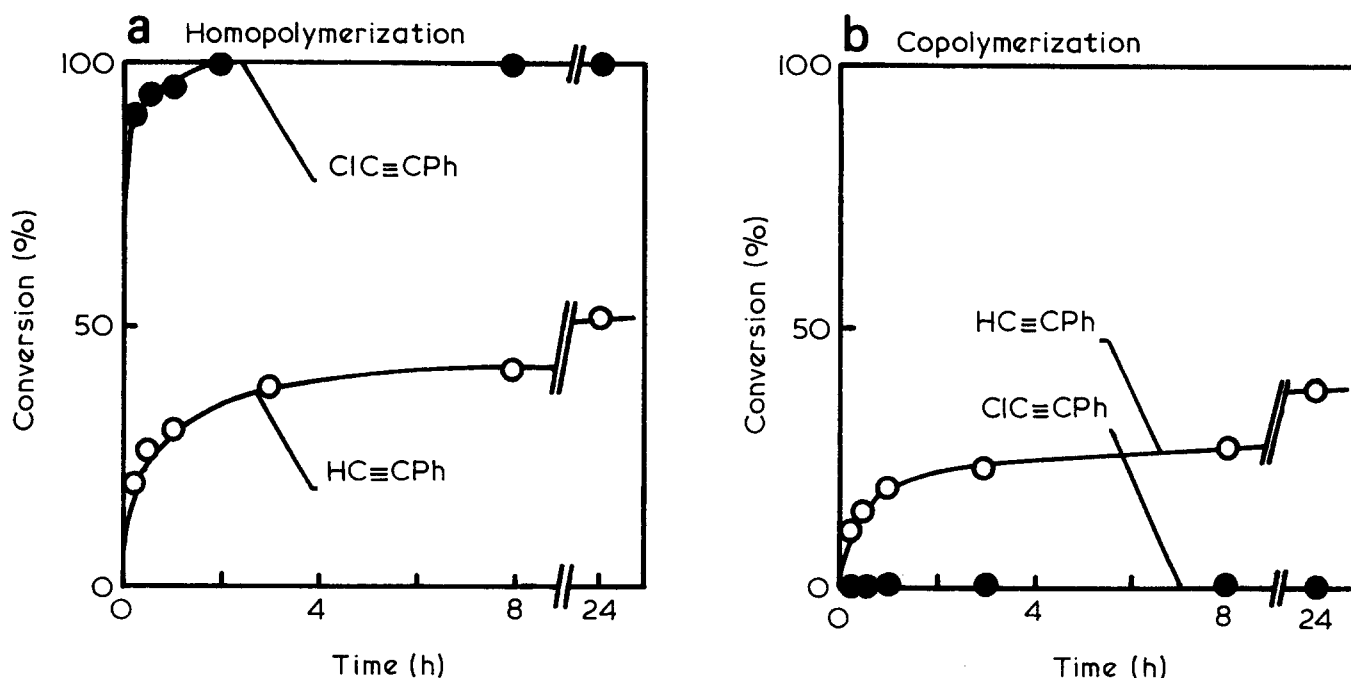


Figure 4 Homo- and copolymerizations of phenylacetylene and 1-chloro-2-phenylacetylene by $\text{MoCl}_5 \cdot n\text{-Bu}_4\text{Sn}$ in toluene at 30°C ($[\text{M}]_{0,\text{total}} = 1.0 \text{ M}$, $[\text{Cat}] = 20 \text{ mM}$)

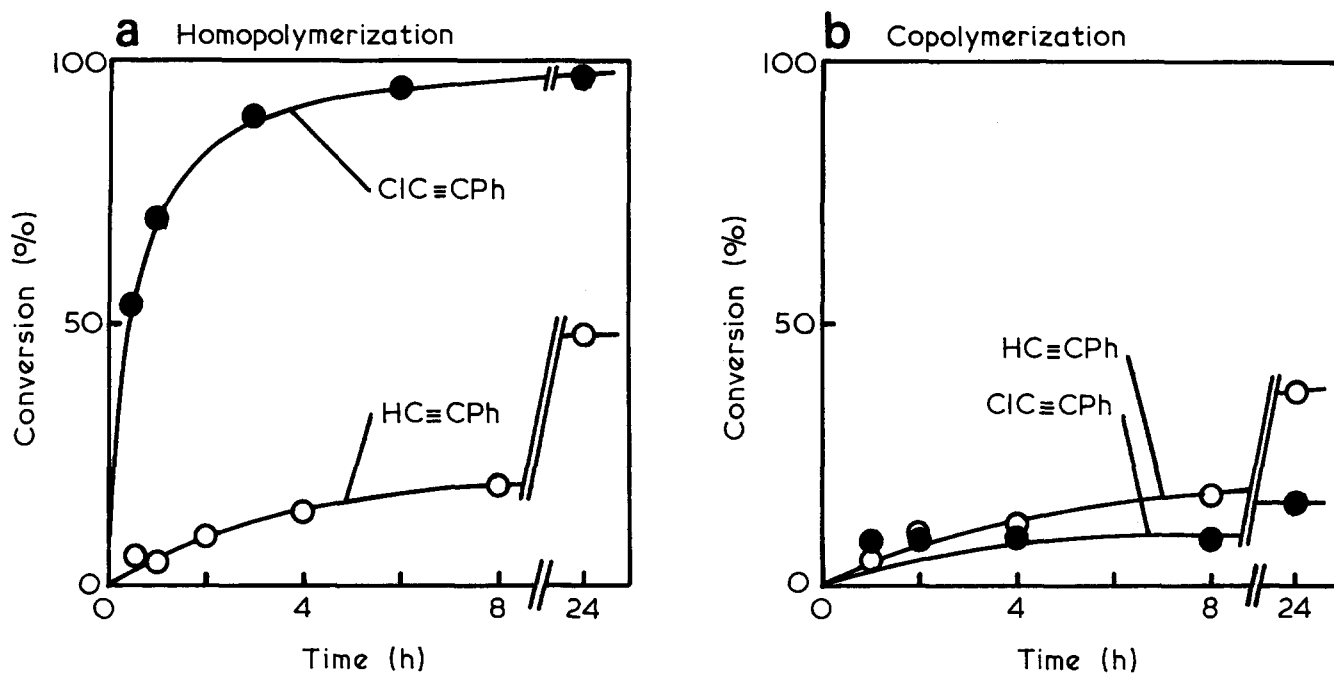


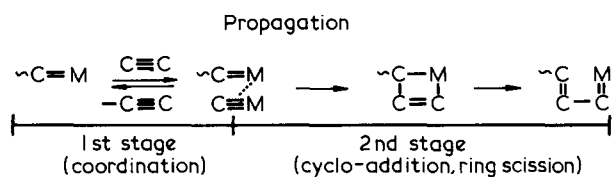
Figure 5 Homo- and copolymerizations of phenylacetylene and 1-chloro-2-phenylacetylene by $\text{Mo}(\text{CO})_6\text{-CCl}_4\text{-}h\nu$ in carbon tetrachloride at 60°C ($[\text{M}]_{0,\text{total}}=1.0\text{ M}$, $[\text{Cat}]=20\text{ mM}$)

These findings demonstrate that a sterically more hindered acetylene shows a lower reactivity in copolymerization, irrespective of their reactivity in homopolymerization.

DISCUSSION

The results in the present study are summarized as follows: (i) the relative reactivity of monomer in copolymerization decreases with increasing steric effect of the substituent(s) in the monomer (the resonance effect is hardly important); (ii) the relative reactivity of monomer in copolymerization is virtually controlled by the steric factor, whereas the reactivity of monomer in homopolymerization is also affected by other factors. Though (i) and (ii) originate from the results using $\text{WCl}_6 \cdot \text{Ph}_4\text{Sn}$ and Mo-based catalysts, respectively, they will not be restricted by such particular catalysts but can be regarded as general features for Mo- and W-catalysed polymerization.

Scheme I depicts a propagation mechanism which



Scheme I

conforms to the observations above. It is likely that the propagation reaction is mediated by a metal carbene^{3,4} and divided into two stages. The first stage is reversible coordination of a monomer to the metal carbene. The second stage consists of cyclo-addition of the coordinated monomer to the metal carbene (formation of a metallacyclobutene) and subsequent scission of the metallacycle formed (regeneration of a metal carbene).

Only the first stage in Scheme I seems to be responsible for the relative reactivity of monomer in copolymeri-

zation: two monomers competitively coordinate to the propagating end. It is reasonable to assume that the coordination ability of the acetylenic monomers is governed mainly by the steric factor. Thus, the result that the steric effect of monomer mainly determines the relative reactivity in copolymerization can be explained in terms of competitive coordination of monomers.

Not only the first but also the second stage in Scheme I should be concerned with the reactivity of monomer in homopolymerization. Since the stability and reactivity of the metallacyclobutene participate in the second stage, the reactivity of monomer in homopolymerization will be affected also by factors other than the steric effect of monomer.

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