

SHORT COMMUNICATIONS

**Polymerization of *m*-Chlorophenylacetylene Initiated by
[Rh(norbornadiene)Cl]₂-Triethylamine Catalyst
Containing Long-Lived Propagation Species**

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In recent years there has been a growing interest in the polymerization of aromatic acetylenes using transition metal catalysts. Several investigations have been described in the literature,¹⁻⁴ including the living polymerization of *ortho* substituted phenylacetylenes by Mo-based catalyst.^{5,6} In this communication we reveal the first polymerization of *m*-chlorophenylacetylene (*m*-CPA) by [Rh(norbornadiene)Cl]₂: [Rh(NBD)Cl]₂ complex cocatalysed with triethylamine (TEA) in chloroform, where long lived propagating species were formed.

In our preliminary experiments, the polymerization of chlorinated phenylacetylenes, for example, *o*-chlorophenylacetylene (*o*-CPA), *m*-chlorophenylacetylene (*m*-CPA) and *p*-chlorophenylacetylene (*p*-CPA) in the presence of Rh complex-TEA catalyst was examined. Among their monomers, *m*-CPA was readily polymerized to quantitative conversion and the polydispersity of the resultant polymer, Poly(*m*-CPA) soluble into common solvents was rather narrow. Therefore, the polymerization of *m*-CPA was studied using three kinds of Rh-based catalysts, *i.e.*, Rh-TEA (1:2), Rh-TEA (1:20), and Rh-TEA (1:100) in order to know in detail the effect of TEA as

the cocatalyst toward the M_w/M_n ratio. When the experiment was carried out in chloroform at 30°C, the polymerization was achieved rapidly with each catalyst, being finished within 1 min. Then monomer was repeatedly supplied several times and was completely consumed in each instance. Among the three Rh-based catalysts, Rh-TEA (1:100) catalyst produced a polymer whose M_w/M_n ratio is as small as 1.68. Molecular weight, M_n , of the poly(*m*-CPA)s obtained in the case of Rh-TEA (1:2), Rh-TEA (1:20), and Rh-TEA (1:100) is plotted as a function of monomer supplied in Figure 1. The polymer molecular weight increased rapidly at low amount of monomer and after that increased progressively with additional monomer. The molecular weight dispersity (MWD) was found to increase slightly throughout this procedure (see Table I). The M_w/M_n ratio for [Rh(NBD)Cl]₂-TEA (1:100) was 1.68 and that for the Rh complex alone was more than 3.0. This suggests the presence of long-lived propagation species in these polymerization systems, as reported by Masuda *et al.*⁵ in the case of chloroalkyne.

This polymerization behaviour is somewhat different from ordinary living polymerization^{5-7,9} because there is no linear relation

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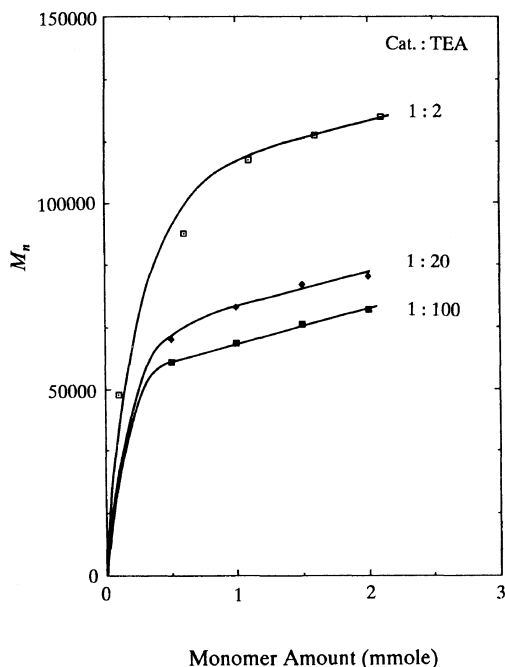
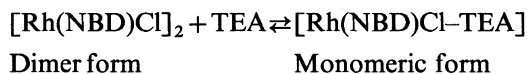


Figure 1. M_n curves of poly(*m*-chlorophenylacetylene) polymerized with Rh-based catalysts in chloroform at 30°C for 1 min. Each monomer solution (1 ml) was fed to catalyst solution. Concentration of monomer solution, $[M]_0 = 0.5$ M; concentration of catalyst solution, $[Cat]_0 = 0.01$ M (5 ml).

between the increase of M_n and amount of monomer supplied or conversion of monomer consumed as can be seen in Figure 1 and Table I. This may be explained in terms of slow dissociation of the Rh catalyst, $[Rh(NBD)Cl]_2$ into a monomeric form, $[Rh(NBD)Cl-TEA]$ where TEA works as a promoter for dissociation and coordinates to the monomeric species as shown below:



The resultant species may be considered to produce an active center responsible for a propagation species in this polymerization system. In fact, the dimer-monomer equilibrium of the Rh-catalyst in chloroform was verified by our preliminary study using 1H

Table I. Polymerization of *m*-chlorophenylacetylene with $[Rh(NBD)Cl]_2$ -TEA catalyst^a

Catalyst	TEA	Monomer	Monomer	M_n	M_w/M_n
			conv.		
mmol	mmol	mmol	%		
0.05	5.0	0.50	100	57000	1.68
		1.00	100	62000	1.71
		1.50	100	67000	1.73
		2.00	100	71000	1.71
		2.50	100	76000	1.74

^a Polymerized with $[Rh(NBD)Cl]_2$ -TEA (1:100) in $CHCl_3$, 30°C, 1 min for each monomer feed. Concentration of monomer solution, $[M]_0 = 0.5$ M; concentration of catalyst solution, $[Cat]_0 = 0.01$ M (5 ml).

NMR and it was shown that the degree of the dissociation changes with the concentration of TEA used.⁸ Therefore, in the case of the highest concentration of TEA, *i.e.*, Rh-TEA (1:100) and low amount of monomer added, the molecular weight, M_n of P(*m*-CPA) does not increase so rapidly with acetylene monomer. The molecular weight, M_n of P(*m*-CPA) obtained must be small because of a rather high concentration of the propagation species, compared to that at the lower ratio, Rh/TEA = 1/2 just as can be seen in Figure 1. Here, it is worth mentioning that the rapid increase of M_n at low amount of monomer supplied can be explained in terms of a relatively slow initiation rate, compared to the rapid propagation rate. Thus TEA works as a useful cocatalyst to produce the propagation species from the rhodium dimer catalyst.

The ratio of the propagating species (P^*) to the Rh catalyst: $[P^*]/[Cat]$, called Initiator Efficiency (I.E.), can be calculated using the equation shown in the literature.⁹ Interestingly, I.E. % was found to progressively increase with increments of the ratio of Rh/TEA and the value reached a plateau, *i.e.*, 22% at high ratio, Rh/TEA = 1/100. This means that in the polymerization by the Rh complex-TEA long-lived propagation species are produced and

increase not only with the addition of monomer but also ratio of Rh/TEA. This causes efficient polymerization of the acetylene monomer, compared to that initiated by the Mo-based catalyst.^{5,6,9}

Here, it would be better to mention the main difference between our results and those of Masuda and Higashimura. In our case, solvents such as ethanol and TEA are useful to give acetylene polymers in high yields. Moreover, TEA works as not only solvent but also as a promoter of the dissociation of the Rh catalyst into the monomeric form, by which *cis-transoidal* polymers are produced selectively.¹⁰ On the other hand, the Mo-based catalyst, so called M.H. catalyst is considered to be deactivated by the amine because of its Lewis acid property. Polymers produced by the Mo catalyst are composed of not only *cis* form but also *trans* form in most cases.¹⁰ Based on these facts, it is concluded that the polymerization mechanism of aromatic acetylenes initiated by the Rh catalyst is different from that initiated by the Mo catalyst,¹¹ from which the formation of metal carbene as an active center is suggested.

Bearing these findings in mind the copolymerization by the Rh complex-TEA using other phenylacetylene derivatives, *i.e.*, *p*-methoxyphenylacetylene (*p*-MeOPA) is also possible. Therefore the preparation of A-B-A or B-A-B type copolymers was attempted with *m*-CPA and *p*-MeOPA. On addition of the second and third feeds of monomers, M_n increased progressively and the M_w/M_n ratio of the block polymer was almost the same as

that of the homopolymers.

Based on all the findings, it may be said that the polymerization involves a long-lived propagating species. Further studies on the behavior of the copolymerization of aromatic acetylenes using the Rh-based catalyst are in progress at our laboratory.

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