Selective Hydrogenation of Phenylacetylene Using Block Copolymer Additional Poisoning Agent

R. Dhamodharan
Department of Chemistry, Indian Institute of Technology, Madras 600 036, India

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A block copolymer, poly (styrene-*block*-4-vinylpyridine) is used as an additional poisoning agent in combination with Lindlar's catalyst to drastically affect the selectivity in the semi-hydrogenation of phenylacetylene. Selectivity is demonstrated from gas chromatography data. The extra advantage in terms of preparing poisoning agent free, very pure and dry monomer are illustrated.

Lindlar catalyst (Pd-$CaCO_3$-PbO) with additional quinoline poisoning agent (a heterogeneous catalyst) is probably the most widely used catalyst in the semi-hydrogenation of alkynes in spite of the fact that many homogeneous hydrogenation catalysts have been developed over the last twenty years.[1] It is widely reported to be effective in the selective preparation of cis-olefins from alkynes.[2] The choice of hydrogenation catalyst for some of the recently reported total syntheses of leukotrienes, prostaglandins, carbohydrates and several other natural products has been Lindlar catalyst. Lindlar and Dubois cite the selective hydrogenation of phenylacetylene to styrene with Lindlar's catalyst in hexane in the presence of quinoline, an additional poisoning agent. However, the same method in the hands of others was not all that selective.[1]

The use of polymers as additional poisoning agents is not known in the literature. Polymer poisoning agents can offer certain unique advantages. For example, the other reaction constituents being solids (with the exception of the solvent) 100% poisoning agent free vinyl monomer can be synthesized from the corresponding acetylinic precursor. This is not possible with the use of small molecular weight additional poisoning agents, such as quinoline, as contamination occurs, often. Such a contamination is likely to affect the polymerization course (rate, termination and chain transfer) as well as the stereochemistry of the product in an ionic or Zeigler-Natta type of polymerization of a vinyl monomer. As an example consider the case of tritium or deuterium labeled phenylacetylene; the labeled styrene molecule formed by semi-hydrogenation can be separated easily from the reaction mixture by a simple distillation process and can be used directly in anionic or other polymerizations which require a very high degree of monomer purity, to prepare labeled polymers of narrow molecular weight distribution (MWD). These polymers are very crucial for quantitating the number of polymer chains and their distribution at interfaces in experiments such as adsorption, interfacial segregation, and interfacial mechanical property investigations.[3] An additional advantage with the use of polymer additional poisoning agent is that the residual solids following monomer distillation after one reaction can be reused with the addition of solvent.

The motivation for this work was a recent paper on polymer adsorption that suggested that the use of a polar polymer might affect the selectivity of a typical Lindlar reduction reaction.[4] To test that idea and to demonstrate the advantages of using a polymer poisoning agent the semi-hydrogenation of phenylacetylene was investigated. The polymer poisoning agent used in this work was poly(styrene-*block*-4-vinylpyridine) (PS-b-4-PVP; number average molecular weight (M_n) ~ 20000; 10 mole percent of styrene). A Hewlett-Packard Gas Chromatograph (GC) with a Super-pac II (GCM084113-1) column was used for the analysis of the product composition. The reaction products were very well separated under the GC conditions used. The experimental details will be published at a later date. It is suffice to say at this point that the time for complete hydrogenation varied with the aging time of the reacting mixture[5] and that the formation of any significant amount of ethylbenzene was not observed, until all the phenylacetylene had reacted.[6]

Table 1. Yield of products as determined by GC in the semi-hydrogenation of phenylacetylene with and without small molecular additional poisoning agent

Entry	Reaction time[c] min	% unreacted PA[a]	Yields of S[a]	Yields of EB[a]
1	t_1=20; t_2=0	3.1	77.8	19.1
2	t_1=20; t_2=10	0.0	33.9	64.1
3[b]	t_1=30; t_2=0	1.6	91.3	7.1
4[b]	t_1=30; t_2=30	0.0	92.1	7.9

[a] PA, S, EB represent phenylacetylene, styrene, and ethylbenzene respectively.
[b] 1 g of quinoline was used as additional poisoning agent.
[c] t_1 is the duration of hydrogenation with a continuous supply of hydrogen (13 psi, T = 22 ± 1 °C) and t_2 is the time during which hydrogenation occurred in the blanket of hydrogen left behind. Typical composition used in the reaction was Lindlar catalyst - 0.15 g; PA - 2.5 ml; Cyclohexane - 60 ml.

The direct hydrogenation of phenylacetylene using Lindlar catalyst results in the simultaneous formation of styrene and ethylbenzene (a consecutive reaction) as shown in Table 1, entry 1. The use of quinoline (an additional poisoning agent) along with the Lindlar catalyst resulted in the formation of 7.9% of ethylbenzene at the stage at which hydrogenation showed a clear break (i.e. at 100% phenyl acetylene conversion) as shown in Table 1, entry 2, in agreement with previous reports.[1]

The use of a block copolymer with a polar adsorbing block, PS-b-4-PVP, as the poisoning agent resulted in a remarkable improvement in the selectivity of the reaction (near 100%), as shown by the results in Table 2, entry 1. The amount of ethylbenzene formed, if any, is below the detection limit, under the gas chromatographic conditions used. Almost identical results were obtained on repetition and these results are shown as

Table 2. Reaction recipe and the product yields as determined by GC in the semi-hydrogenation of phenylacetylene with polymer poisoning agent

Entry	Reaction time[c]	% unreacted	Yields of	
	min	PA[a]	S[a]	EB[a]
1[d]	t_1=12; t_2=185	3.5	96.5	0.0
	t_1=12; t_2=210	0.0	100.0	0.0
2[d]	t_1=12; t_2=210	5.5	94.5	0.0
	t_1=12; t_2=220	0.0	100.0	0.0
3[e]	t_1 = 73 min	0.0	98.3	1.7

[a, c] Abbreviations are the same as in Table 1.

[d] 0.38 g of poly(styrene-b-4-vinylpyridine) was used.

[e] reaction mixture was not aged before hydrogenation.

entry 2 in Table 2. Similar results were also obtained, if the reaction mixture was not aged before the addition of hydrogen and this is shown as entry 3 in Table 2. In this case, the hydrogenation rate slowed down but the selectivity was not affected markedly.[5] If the reduction reaction were carried out after all the phenylacetylene had been depleted from the surface (beyond 100% styrene formation) ethylbenzene is formed.[6] Therefore to preserve the selectivity obtained in the first stage of the reduction it is necessary that the reaction be stopped (by the flushing of the hydrogen gas from the reaction mixture) after all the phenylacetylene molecules have been semi-hydrogenated.

The mechanism of heterogeneous hydrogenation of alkynes is not thoroughly understood.[1] We speculate that the selectivity observed might be due to preferential interaction (in terms of free energy) of 4-vinylpyridine and phenylacetylene with the catalyst surface.

Lindlar catalyst (Pd-$CaCO_3$-PbO) with an additional block copolymer poisoning agent results in near 100% selectivity in the semi-hydrogenation of phenylacetylene.[7] To the best of the authors knowledge this is the first work illustrating the unique use of polymer poisoning agents. The methodology presented in this paper will have important ramification in current research areas such as natural product synthesis and ultra pure monomer synthesis from acetylinic precursors (in turn for stereoregular and living polymer syntheses).

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References and Notes

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5 Aging time is the period between the mixing of reaction ingredients and the introduction of hydrogen. Unless specified an aging period of 12 h was allowed.

6 A reduction reaction carried out for 3 min beyond 100% phenylacetylene conversion resulted in the formation of 49.1% styrene and 50.9% ethylbenzene.

7 Very pure tritiated styrene, obtained from the hydrogenation mixture by a simple trap to trap distillation, was polymerized anionically in benzene using *sec*-butyllithium as the initiator. Our aim was to prepare polystyrenes of M_n 10000 and 140000 with narrow MWD and we obtained polymers of M_n and MWD (within brackets) 11821 (1.03) and 143972 (1.06) confirming that very pure styrene as required by the limits of anionic polymerization is produced using the present method.