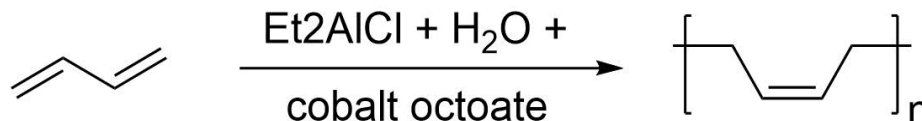


# *cis*-1,4-Polybutadiene by Cobalt-Aluminum-Water Catalysis

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## 1. Procedure (Note 1)

Two clean 12 oz and three 28 oz beverage bottles are dried in a 110° oven overnight. While purging the bottles with nitrogen (Note 2, Figure 1), they are capped with unlined bottle caps having fitted rubber liners (Note 3) and a center puncture seal to admit a syringe needle. The bottles are pressurized to 15 psig with nitrogen (Note 4) and set aside.

Benzene (2.5 l, Note 5) is distilled at 10 torr pressure (Note 6) through a closed, nitrogen-purged apparatus having ground glass joints throughout (Figure 2). The first 10% of distillate is discarded (Note 7). Distillation under nitrogen is continued, 2.0 l of the benzene being collected in a 3 l nitrogen-purged round-bottomed flask of the type shown in Figure 2. The receiver is disconnected and attached to a 12 x 1.5 in column filled with activated silica-gel (Note 8) through which nitrogen was previously passed for 15 min. The first 500 ml of percolate is discarded, and the next liter of benzene is collected in another flask of the type shown. The silica-gel column is disconnected, and the flask containing the purified benzene is connected to the Hg trap. Under continuous nitrogen pressure, 250 ml of the purified benzene is collected in one dry 28 oz bottle (Note 9) to which about 15 g of granular  $\text{CaH}_2$  of 4-40 mesh is added. While purging with nitrogen, a bake-dried, glass-wool plug is inserted into the neck of the bottle, which is then capped with a rubber lined cap, pressurized to 15 psig and let stand overnight (bottle A). In a second dry 28 oz bottle, 518 ml of benzene is collected, about 15 g of  $\text{CaH}_2$  is added, and the bottle is capped while purging (bottle B). In a clean 12 oz beverage bottle about 0.1 l of the benzene is collected, 2 ml of distilled  $\text{H}_2\text{O}$  is added, the bottle is capped, pressurized, and set aside overnight (bottle C).

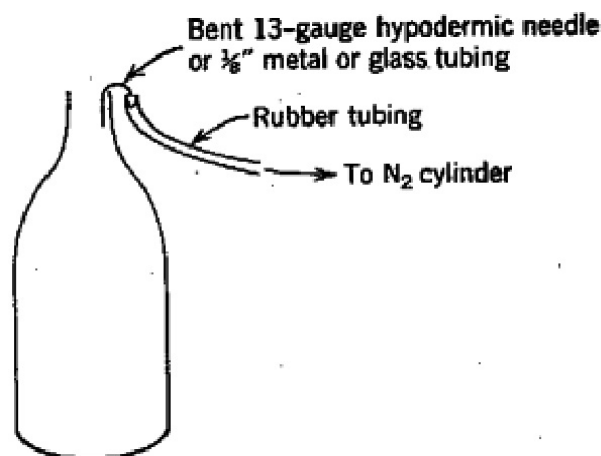
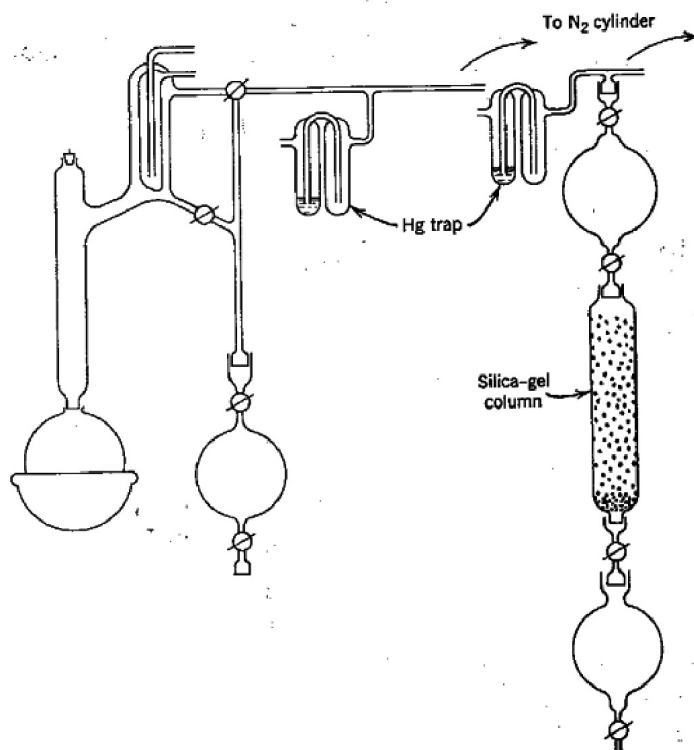


Figure 1. Bottle purging method.



**Figure 2.** Benzene purification apparatus.

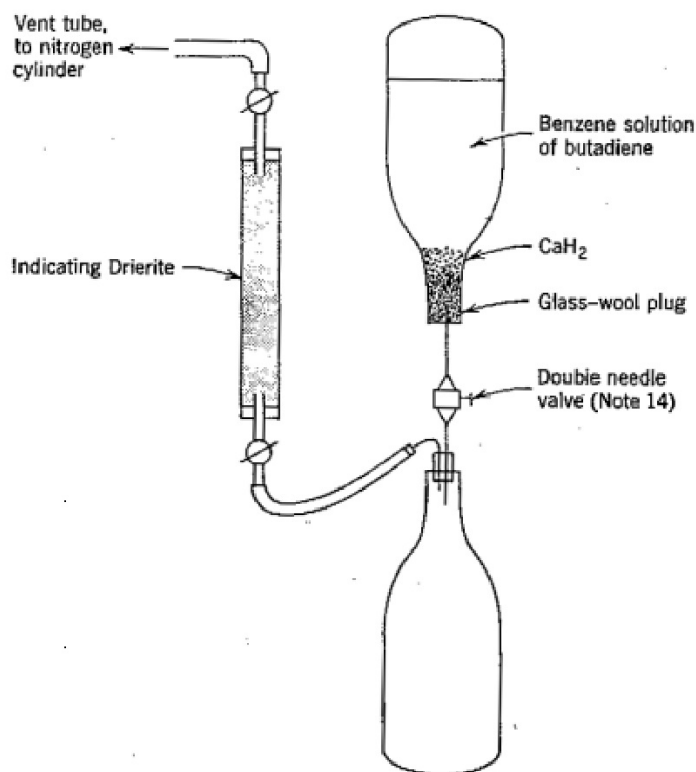
One-half liter of at least 99% pure butadiene (Note 10) is distilled (using solid  $\text{CO}_2$ -acetone in the condensing head) with a 100 g fore-run collected in a hydrocarbon solvent discarded. The receiver is now removed, and bottle B, containing the benzene solvent and  $\text{CaH}_2$ , is uncapped and inserted into the receiver position. Distillation is continued until 88 ml of butadiene (50 g) is collected. The bottle is recapped, pressurized, and set aside overnight.

The next day, an approximately 1M solution of diethylaluminum chloride (Note 11) is prepared as follows: A dried, pressurized 12 oz bottle is punctured through the rubber gasket with an 18-gauge needle until the pressure is vented. Dry benzene (87.4 ml) from bottle A is withdrawn by means of a syringe needle carefully inserted through the cap of the inverted bottle (Note 12) and injected through the rubber liner into the 12 oz bottle. This bottle is now weighed to the nearest 0.1 g. Next, approximately 13 ml of diethylaluminum chloride is transferred to the bottle (Note 13), which is reweighed and repressurized. The molarity is calculated from the weight of added diethylaluminum chloride and the total volume of solution.

A solution approximately 0.02M in cobalt octoate is prepared as follows: If the commercial preparation of 12% cobaltous octoate (Note 14) is used, 1 ml of the solution contained in a 2 ml syringe fitted with a needle and needle valve, is weighed on an analytical balance and set aside. A dry 12 oz bottle is punctured through the rubber liner with an 18 gauge needle until the pressure is relieved. Dry benzene (0.1 l) from bottle A is injected into the bottle with a 50 ml syringe. The cobaltous octoate is then injected, the bottle capped and repressurized. The syringe is weighed again, the weight of cobaltous octoate taken, and the molarity for the given volume of solution is calculated.

The bottle containing the benzene solution of butadiene is vented and opened, and, while purging with nitrogen, a bake-dried glass-wool plug is packed into the neck of the bottle. The bottle is capped and set into position in the apparatus shown in Figure 3. A dry 28 oz receiver bottle is

vented and, while being purged with nitrogen, is forced onto the rubber stopper attached to the lower needle (Note 15). With the needle valve open, a positive nitrogen pressure is admitted into the bottle of solution via the vent tube. The tube is disconnected from the nitrogen cylinder, and the open end is placed in the hood. The solution will flow into the receiver as long as a slight pressure of nitrogen is maintained above it.



**Figure 3.** Solution transfer apparatus.

After 551 ml of the solution has been transferred (Note 16), the needle valve is closed, the nitrogen purge needle is quickly inserted into the receiver bottle, which is then capped with a cork-filled cap to which an aluminum disk 0.004 in thick is snugly fitted. The bottle containing the solution is chilled in a 5° bath for 1-2 h. It is then removed, uncapped, and, while being purged with nitrogen, 10 mmol of diethylaluminum chloride is added, using a syringe and needle to make the transfer. Similarly, 30 ml of the benzene solution of H<sub>2</sub>O from bottle C (Note 17) is added, followed by 0.02 mmol of the cobaltous octoate. The bottle is capped with an aluminum disk-containing, cork-filled liner cap, placed in a bottle guard, and rotated end over end in a constant temperature bath at 5°.

Although polymerization may be complete in 4-6 h, it is best to allow the reaction to proceed overnight. The bottle is scored and carefully cracked open. The viscous polymerizate is transferred with a minimum of exposure to air to a 3 l beaker or gallon jar filled with about 2 l of isopropanol containing 1.0 g of antioxidant (Note 18). After several minutes of agitation in the alcohol, the polymer is removed piecewise and placed in a screw-cap quart jar half-filled with isopropanol in which 1.0 g of the antioxidant is dissolved. The next day the polymer is removed, blotted dry between absorbent paper towels or clean cloth, and then dried in a 50° vacuum oven overnight; yield of polymer approximately 50 g.

## 2. Characterization

The dilute solution viscosity of *cis*-1,4-polybutadiene determined in toluene at 25° is 4.5-6.0 dl/g which corresponds to a molecular weight of about 500,000. The polymer is free of any gel, as determined by filtering through a 100-mesh wire screen a solution of 0.4 g of polymer in 100 ml of toluene. The *cis*-1,4 content of the polybutadiene is 98% as measured by the film technique described in the literature.<sup>3</sup> The influence of polymerization variables upon the polymer and procedure have been described in the published literature.<sup>4</sup>

## 3. Notes

1. The preparation of polybutadiene having the characteristics described here requires manipulative procedures that rigorously exclude access of atmospheric moisture and oxygen to the reacting materials. The diethylaluminum chloride must be pure and free of any previous contact with moisture, air, or aluminum metal. Small variations in the water content of the system will affect the *cis*-1,4 content and the polymer viscosity. A large excess of water leads to highly gelled polymer. Insufficient or complete absence of water results in little or no polymer formation.
2. High purity nitrogen of maximum 5 ppm H<sub>2</sub>O and oxygen impurity should be used.
3. Standard rubber cap liners, NO. 3582-11-1579, are available from Firestone Industrial Products Company, Noblesville, Indiana, to be used with the unlined crown caps.
4. The hot bottles are pressurized with an 18 gauge hypodermic needle attached to rubber pressure tubing connected to the nitrogen cylinder. Pressure adjustment to 15 psig at intervals during cooling of the bottles to room temperature will be necessary.
5. ACS reagent grade, thiophene-free benzene is used.
6. The Hg traps shown in Figure 2 contain mercury to a distance of 10 mm above the tip of the inner tube.
7. This contains the major amount of H<sub>2</sub>O contaminant.
8. Mesh size 28-200.
9. Volumes to which bottles are to be filled can be estimated with sufficient accuracy by measuring the height of a required volume of the same liquid contained in another bottle of the same size, and making a wax pencil mark on the receiver bottle.
10. Butadiene obtained from Phillips Petroleum Company was used. It must be relatively dry even before distillation. It is recommended that a flask containing the butadiene be chilled in solid CO<sub>2</sub> to freeze most of the contaminant H<sub>2</sub>O, and that the butadiene then be transferred to the distillation flask through cotton gauze.
11. The product of Ethyl Corporation or Texas Alkyls, Inc., is suitable.
12. Care must be taken not to penetrate the glass-wool plug beyond the point where particles of CaH<sub>2</sub> may enter the syringe. Using a 50 ml syringe, it will be necessary to make two transfers.
13. The technique of transferring the alkylaluminum should conform to the instructions issued by the manufacturer. Twenty-five percent by weight diethylaluminum chloride in toluene is commercially available and may be used without dilution; 5.4 ml of this solution contains 10 mmol of the alkylaluminum.
14. Cobaltous octoate from Witco Chemical Company, Inc., was used; percent based on cobalt.
15. A 1/8 in bar stock stainless steel needle valve to which a 1/8 in brass nipple is silver-soldered at each end. A hypodermic syringe lock tip is silver-soldered to each nipple. A suitable equivalent valve assembly may be used.
16. The transferred solution contains 50 g of butadiene.
17. This contains 1.0 mmol of dissolved H<sub>2</sub>O at room temperature. A valve-fitted needle is inserted through the rubber liner of bottle C, the bottle is carefully inverted so the excess H<sub>2</sub>O flows down past the needle into the neck of the bottle. After allowing about 30 min for the settling of finely dispersed H<sub>2</sub>O, the needle valve is opened to permit 5-10 ml of the solution to be

discarded. A 50 ml syringe is attached to the needle valve, and 30 ml of the solution is withdrawn.

18. Phenyl- $\beta$ -naphthylamine is suitable. Other known rubber antioxidants may be used.

#### 4. Methods of Preparation

*cis*-1,4-Polybutadiene can also be made with  $\text{Et}_2\text{AlCl}$ ,  $\text{H}_2\text{O}$ , and other types of cobalt compounds, such as cobalt acetylacetonate, cobalt naphthenate, cobalt stearate, or cobalt chloride, the latter preferably rendered soluble through its dipyrindyl complex.<sup>4</sup> Another suitable catalyst consists of  $\text{Et}_2\text{AlCl}$  and cobalt octoate or other cobalt compound with certain organic compounds as substitutes for  $\text{H}_2\text{O}$ , such as cumene hydroperoxide or *t*-butyl chloride.<sup>5</sup> Still another method uses mixtures of  $\text{Et}_3\text{Al}$  and  $\text{AlCl}_3$ , or  $\text{Et}_2\text{AlCl}$  and  $\text{EtAlCl}_2$ .<sup>5</sup>

#### 5. References

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