cis-1,4-Polyisoprene by Aluminum-Titanium Coordination Catalysis

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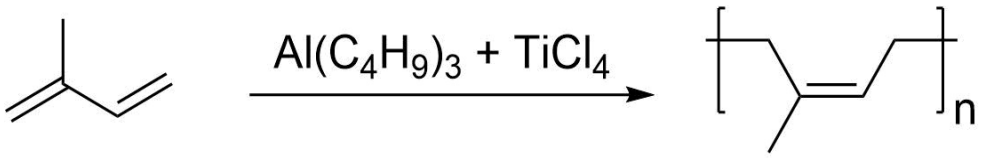

1. Procedure

To a carefully cleaned and dried 4 oz, narrow-mouthed, screw-cap bottle (Note 1) is added 55 g of a 15% by weight isoprene (Note 2) solution in pentane (Note 3). The solution should be taken directly from the exit of a jacketed column packed with silica gel (Note 4). Approximately 5 g of the solution is vented by heating the uncapped bottle on a hot sand bath (Note 5). After 0.200 mmol of triisobutyl aluminum and 0.185 mmol of titanium tetrachloride in heptane (Notes 3 and 6) are added to the bottle with syringes (Notes 7 and 8), the bottle is sealed with a cap having an inner Teflon lining and is allowed to rotate for 16 h in a 50° water bath. The bottle is removed, allowed to cool, and 10 ml of a dilute solution of antioxidant (Note 9) is added to it. The contents of the bottle are then poured into a beaker containing 200 ml of a 1% solution of antioxidant in isopropyl alcohol. The coagulated material is dried at 40° under vacuum to give a polymer in 70-80% yield having an inherent viscosity[3,4] of 2.0-3.5. The *cis* content of the polymer should be better than 94% when analyzed according to the method of Binder.[5]

2. Notes

1. All apparatus should be clean and thoroughly dry.
2. Phillips polymerization grade isoprene is used after flash distillation under nitrogen just before use. The isoprene should be low in α-acetylenes, cyclopentadiene, 2-butyne, and any oxygen- or sulfur-containing compounds. Even within the specification limits for this high purity isoprene there may be variations in the isoprene quality that lead to induction periods and slow reaction rates. The isoprene may require preliminary treatment to remove these adventitious impurities. After distillation, isoprene should not be stored for long periods without addition of about 200 ppm of *t*-butylcatechol as oxidation inhibitor.
3. Phillips pure grade (99+%) pentane or heptane should be washed with concentrated sulfuric acid until no further discoloration takes place. After neutralizing and drying, the solvent is flash-distilled and stored over sodium until used.
4. A column 3/4 in in diameter and 13 in long containing about 60 g of silica gel is suitable; a cooling jacket is necessary to avoid polymerization in the column. It is convenient to use a graduated, cylindrical separatory funnel at the top of the column. Activated silica gel, 28-200 mesh size from the Davison Chemical Division of W. R. Grace and Co., is satisfactory. The column should be flushed with nitrogen and rinsed with 100 ml of dry pentane before use.
5. A glass rod is placed in the bottle to prevent bumping.
6. Dilute solutions (0.2-0.5*M*) of triisobutyl aluminum and titanium tetrachloride are conveniently prepared in heptane and stored under nitrogen in 4- or 8-oz narrow-mouthed bottles fitted with septa or with holed metal caps having an inner self-sealing gasket made of butyl rubber. The

quantities needed may then be conveniently withdrawn and transferred by syringe. Triisobutyl aluminum from Ethyl Corporation or Stauffer Chemical Company is satisfactory without further purification. *Caution! Both alkyl aluminum and titanium tetrachloride react vigorously with oxygen and water and should be handled in a dry box in a nitrogen or other inert gas atmosphere.*

7. A separate syringe should be used for each solution.
8. Slight variations in the Al/Ti mole ratios may be necessary to compensate for the triisobutyl aluminum used to destroy residual air and water in the reaction mixture. The total catalyst corresponds to about 0.8 g per 100 g of monomer.
9. This is to protect the polymer and destroy the catalyst without coagulation. Any hydrocarbon solvent may be used in which the antioxidant is soluble or in which it may be suspended. Di-(*t*-amyl)-hydroquinone or other standard rubber antioxidant may be used. A solution containing 10 ml of isopropyl alcohol and 2.0 g of antioxidant per 100 ml of benzene is satisfactory.

3. Methods of Preparation

cis-Polyisoprene has been prepared with this catalyst system[6] and with a lithium or lithium alkyl catalyst.[7] The polymers prepared with lithium catalysts have somewhat lower *cis* contents and may be readily prepared to higher inherent viscosities and lower gels.

4. References

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