trans-1,4-Polyisoprene by Aluminum-Titanium-Vandium Catalysis

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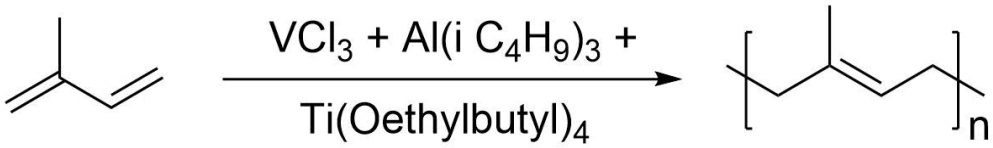

1. Procedure

Caution! Triisobutyl aluminum is pyrophoric and reacts violently with water. The vanadium compounds are toxic.

The Catalyst. In a 250 ml, three-necked flask fitted with a condenser, mechanical stirrer, and inert gas inlet (Notes 1 and 2) are placed 8.0 g of kaolin (Note 3) previously dried at 120° for 16 h, 70 ml of dry benzene (Note 4), and 2.72 g (1.5 ml) of vanadium tetrachloride in 15 ml of dry benzene (Note 5). The mixture is stirred gently and refluxed for 3 h in a fume hood. All operations are conducted under flowing inert gas. The mixture is allowed to cool to room temperature, filtered on a sintered glass funnel, washed with several volumes of dry benzene, transferred to a suitable container, and dried under vacuum (1 torr for 24 h, Note 6). The supported vanadium trichloride is analyzed for chlorine by the Volhard method. The product should have a VCl_3 content of 18-20%.

Polymerization. In a dry, heavy-walled glass container (Note 7) of at least 600 ml capacity are placed, in the order given, 150 ml of dry benzene, an amount of the VCl_3 on clay equivalent to 70 mg (0.445 mmol) of VCl_3, tetra-2-ethylbutyl titanate (0.1 ml, 0.22mmol) in 10 ml of dry benzene (Note 8), triisobutyl aluminum (1.15 ml, 4.45 mmol) in 10 ml of dry benzene (Note 9), and 150 ml (100 g) of isoprene (Notes 10 and 11). The container is sealed (Note 7), vigorously shaken by hand a few times and then agitated (by rocking or shaking) in a 50° bath for 6 h (Note 12). The container is allowed to cool to room temperature, the highly swollen polymer is removed (Note 13), cut into small chunks, and placed in 1 l of methanol containing 2 g of a phenolic antioxidant. The polymer is then shredded in a large explosion-proof blender in the presence of methanol plus antioxidant. The polymer is soaked in 1 l of fresh methanol plus antioxidant for a few hours, filtered, and dried in a vacuum oven at 40° overnight. The yield of *trans*-polyisoprene is 90-100 g (90-100%).

The polymer is identical with natural balata in its x-ray diffraction pattern and dilatometric melting points (56° and 64°). The infrared spectrum of the synthetic polymer is almost identical with that of natural balata, the former sometimes having some *cis*-1,4-content. The polymer as obtained is slightly gelled. This gel can be broken down easily by milling on a two-roll rubber mill for a few minutes at 110-120° roll temperature. The polymer after milling is completely soluble in solvents such as benzene and is of far higher molecular weight than natural balata. Its intrinsic viscosity in benzene at 30° equals 3-5 dl/g versus 0.8-1.0 dl/g for the natural polymer. Mooney viscosity ML-4 at 100° equals 80-100 versus 10-20 for natural balata.

2. Notes

1. All glassware and auxiliary equipment used in the preparation of the catalyst and in the polymerization should be dried at 120° for at least 4 h before use and cooled in a dry inert atmosphere.
2. Dry argon or nitrogen is suitable.
3. The kaolin, Continental Clay, was obtained from R. T. Vanderbilt Company. The specific surface area is 10 m^2/g.
4. Reagent grade benzene containing less than 10 ppm of water was used. Passage through a column of silica gel surmounted by a layer of vegetable charcoal with collection and storage under a dry inert atmosphere over sodium or Linde 4A Molecular Sieves suffices.
5. *Caution! VCl_4 stored in glass should be kept cool and in the dark. Storage of the glass container in a metal can containing limestone or the like is suggested because samples of VCl_4 have been known to decompose in storage to vanadium trichloride and chlorine rapidly enough to shatter glass containers.*
6. The filtration and transfer are conveniently carried out in a dry, inert atmosphere glove box. The vacuum is broken by admitting a dry inert gas. Storage is under a dry inert gas.
7. An ordinary soda bottle to be sealed with a crown cap is suitable. The bottle should be unscratched. The gasket in the crown cap may be nylon, polyethylene, or Teflon of suitable thickness.
8. Equimolar amounts of any tetraalkyl titanate may be used. The isopropyl and higher esters are used as commercially available. The ethyl and methyl ester should be distilled before use.
9. The triisobutyl aluminum is commercially available and used without purification. Twenty percent solutions of triisobutyl aluminum in benzene are commercially available.
10. Polymerization grade isoprene (Phillips Petroleum Company, Special Products Division) distilled from sodium or purified by passage through a 3/1 mixture of silica/alumina is suitable. In the silica/alumina purification, care should be taken to avoid excessive heat on first wetting the absorbent. Inert gas blankets are used throughout purification and storage.
11. Additions to the polymerization vessel are made under an inert atmosphere with syringes and needles. The solid VCl_3 is conveniently weighed into a small, dry Erlenmeyer flask and transferred to the polymerization vessel with a dry powder funnel.
12. As short a time as is practicable should elapse between addition of the trialkyl aluminum and the isoprene. The container should be sealed very shortly after the isoprene addition and placed in the 50° bath immediately thereafter.
13. It is necessary to break the soda bottle to remove the polymer.

3. References

1. *Research Center, United States Rubber Company, Wayne, NJ 07470, Contribution No. 249.*
2. *The Goodyear Tire & Rubber Company, Akron, OH 44309.*