High Density Polyethylene

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$$H_2C{=}CH_2 \xrightarrow{\text{TiCl}_4 + \text{Al(C}_2\text{H}_5)_3} {\left[\!\!-CH_2{\cdot}CH_2-\!\!\right]}_n$$

$$H_2C{=}CH_2 \xrightarrow{\text{AlBr}_3 + \text{VX}_n + \text{Sn(C}_6\text{H}_5)_4} {\left[\!\!-CH_2{\cdot}CH_2-\!\!\right]}_n$$
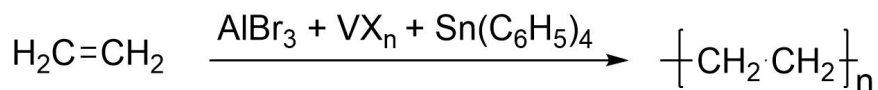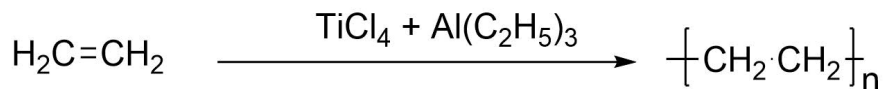
A. Polymerization with Al/Ti Catalyst
1. Procedure

   A 2 l, three-necked, round-bottomed flask is suspended in a water (or oil) bath held at 60°. It is then fitted with a reflux condenser, mechanical stirrer, and gas inlet tube reaching to the bottom of the flask. One opening is sealed with a septum to permit injecting the catalyst slurry (Note 1). The flask is then charged with 1 l of Phillips ASTM grade *n*-heptane and purged with dry nitrogen for 1 h to remove water and other volatile impurities (Note 2).

   While the reaction flask is being purged, a 100 ml bottle is charged with about 25 ml of dry *n*-heptane and a magnetic stirring bar, purged with dry nitrogen, and sealed with a septum. By way of syringes, 4.65 mmol of titanium tetrachloride and 2.0 mmols of triethylaluminum are added to the bottle as dilute solutions in heptane (Note 3). The total volume of heptane should now be about 40 ml. A colloidal brown precipitate deposits as the co-catalysts interact, and the slurry is stirred on a magnetic stirrer for 30 min at room temperature.

   The nitrogen purge through the reactor is discontinued, and ethylene is admitted at the rate of 3-4 l/min. The aged catalyst slurry described above is then injected into the reactor with a syringe to start the reaction. Polymerization begins immediately with the evolution of heat, and particles of polyethylene are observed. After addition of the catalyst, the ethylene flow is gradually reduced to 2 l/min (Note 4). At the end of 1 h the reaction is stopped by the addition of 50 ml of isopropanol to inactivate the catalyst. The resulting white polymer is separated by filtration, boiled in 1 l of isopropanol, recovered by filtration, and dried overnight in a vacuum oven at 70°. The yield is 65 g of polyethylene in the form of a fluffy white powder. This polymer has a melting point of 128°, (as determined by disappearance of birefringence), melt index (ASTM D-1238-52T) of 1-2 (Note 5), and an intrinsic viscosity of 1.5-2.0 dl/g. The polymer is soluble in boiling xylene or other hydrocarbon solvents at temperatures above 130°. Above its melting point it can be compression molded into films suitable for physical testing or infrared spectroscopy. In the subsequent discussion of the infrared spectrum, this polymer will be designated Sample A.

2. Notes

  1. The glassware should be dried in an oven at >100°, assembled while warm, and immediately purged with nitrogen. Joints should be greased with a minimum of lubricant to prevent contamination, and the stirrer must be sealed to prevent air from entering the reactor.
  2. A desirable additional step is to purge the diluent overnight in a separate flask with a slow stream of dry nitrogen and transfer it to the reactor through a glass or polyethylene tube without exposure to air.

     If ASTM grade *n*-heptane is not available, heptane of unknown purity can be refined by stirring with concentrated sulfuric acid overnight, washing several times with water, drying over

calcium hydride, and passing it through alumina. Cyclohexane of equivalent purity may be substituted for *n*-heptane.

   Pure ethylene is also desirable. Phillips ethylene (99 mol% minimum) was used here.

3. *Caution! Aluminum triethyl spontaneously ignites in air and must always be handled in an inert atmosphere.* Dilute solutions of triethylaluminum and titanium tetrachloride should be prepared in a dry box at a concentration of 0.5 mmol/ml, and then handled only with dry syringes.

4. When the catalyst is first added, polymerization may be so rapid that ethylene concentration in the reactor is depleted and air is sucked in. A bubbler may be attached to the exit from the condenser to show that an excess of ethylene is always passing through the system.
   Caution! This should be carried out in a good hood to carry away excess ethylene.

5. The polymer melt index is inversely proportional to the Al/Ti ratio, and the melt index may be varied over a considerable range by fairly small changes in the Al/Ti ratio.

B. Polymerization with $AlBr_3$ + VX_n + $Sn(C_6H_5)_4$ Catalyst

1. Procedure

   The polymerization apparatus described for part A is assembled and the reactor is charged with 1 l of purified cyclohexane (or *n*-heptane) and 2 mmols of tetraphenyltin, and purged with dry nitrogen as before (Note 1). A flow of Matheson C. P. ethylene (Important! see Note 2) is started at 3-4 l/min, and then 5 mg of vanadium tetrachloride (or vanadium oxytrichloride) and 4 mmol of aluminum bromide (Notes 3 and 4) are added by syringes as dilute solutions in cyclohexane. Polymerization begins as soon as the last catalyst component is added, and white polyethylene particles may be observed almost immediately. The ethylene flow is then reduced to 2 l/min over an interval of 3-5 min. The reactor contents should remain white or very light tan throughout the experiment. A brown color indicates contamination.

   At the end of 1 h, the reaction is stopped by the addition of 50 ml of isopropanol. The polymer is separated by filtration, boiled in 1 l of isopropanol, recovered by filtration (a second extraction may be required), and dried overnight in a vacuum oven at 70°. The yield is 40 g of white particulate polyethylene having a melting point of 136°, melt index (ASTM D-1238-52T) of 0.0-0.1, and an intrinsic viscosity of 2-3 dl/g in tetralin at 130°. This polymer is called sample B in the discussion of polymer structure.

2. Notes

1. This catalyst is more sensitive to contamination than the titanium catalyst, and the precautions mentioned in part A should all be carefully followed.

2. This particular catalyst *requires* a trace of oxygen in the ethylene for sustained polymerization. The reason for specifying Matheson C. P. ethylene is that this gas consistently contains about 400-600 ppm of oxygen which is about the optimum range for the $AlBr_3$-VX_n-$Sn(C_6H_5)_4$ catalyst. Significantly higher or lower oxygen concentrations lead to reduced yields of polymer and changes in the polymer end groups.[3] Ethylene from some sources does not contain enough oxygen for good polymerization results with this catalyst. In these cases 400-600 ppm of oxygen can be metered into the ethylene to achieve good polymerization activity. However, this technique is difficult and requires specialized equipment.

3. The vanadium halide and aluminum bromide solutions should be prepared in a dry box and handled by hypodermic syringes. Tetraphenyltin is stable in air and may be added to the reactor as a solid.

4. Aluminum chloride is equivalent to aluminum bromide as a cocatalyst and may be substituted for it. A saturated solution of aluminum chloride in boiling cyclohexane contains about 6 g/l of $AlCl_3$ and may be prepared by refluxing a ten-fold excess of aluminum chloride in cyclohexane under a nitrogen atmosphere. Solutions prepared this way usually contain some colloidal

aluminum chloride which need not be separated from the solution. An aliquot of the hot solution is used directly for the polymerization.

3. Polymer Structure

The polyethylene from part A [$Al(C_2H_5)_3$ plus $TiCl_4$ catalyst] is more branched than the polyethylene from part B [$AlBr_3$ + VX_n + $Sn(C_6H_5)_4$ catalyst]. Curve 1 in Figure 1 is the infrared spectrum of sample A. Curve 2 is the spectrum of sample A compensated against sample B from 7 to 7.5μ, which shows the substantially stronger methyl group absorption at 7.25μ in sample A. Curve 3 gives the spectrum of sample B from 8 to 13μ and shows that the double bonds found in sample A are missing in sample B.

These data clearly illustrate the subtle changes in polymer structure caused by different catalyst formulations and show the utility of infrared spectroscopy in detecting them.

4. Methods of Preparation

The Ziegler-type catalyts[4] normally consist of a reactive metal alkyl in combination with a transition metal compound of Groups IV to VI in the Periodic Table (Ti, V, Cr). Some other typical combinations that are active catalysts for olefin polymerization are AlR_3 + $TiCl_3$, AlR_3 + VCl_3, AlR_3 + $VOCl_3$, R_2AlCl + VCl_4, R_2AlCl + $VOCl_3$. More extensive lists of catalytically active systems are given elsewhere.[5,6,7,8] The simple procedures described above are suitable for qualitative work with many of these systems. Generally, the yield or molecular weight, or both, of the polymer are significantly influenced by polar impurities, such as water or oxygen, which may be present in the system in the parts-per-million range.[3,9] A quantitative study, such as a kinetic analysis, is meaningless unless all polar impurities in the system are rigorously monitored and controlled.
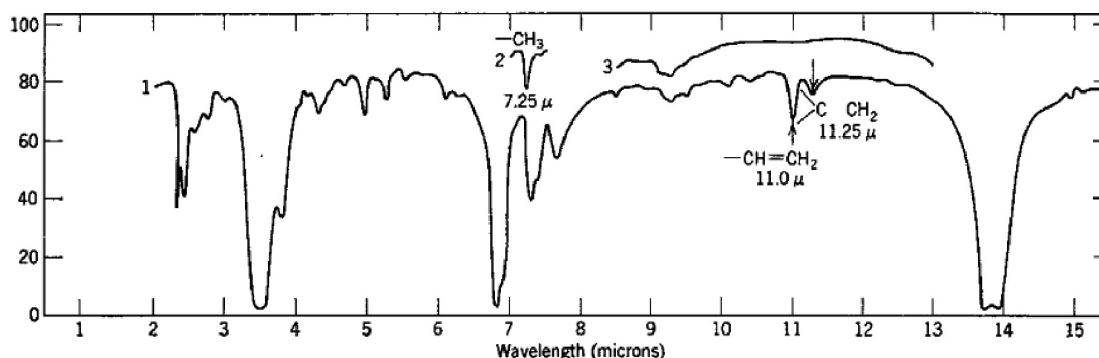

Figure 1. Infrared spectra of polyethylenes. Curve 1, sample A, 6 mils thick; curve 2, sample A compensated against sample B, 7-7.5μ; curve 3, sample B, 8-13μ.

5. References

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