Cationic Transannular Polymerization of Norbornadiene to Polynortricyclene

Submitted by: J. P. Kennedy
Checked by: W. A. Thaler

1. Procedure

Into a 100 mL, three-necked, round-bottomed flask fitted with a stirrer and thermocouple are added, under nitrogen atmosphere in a dry box, 10.14 g of norbornadiene [bicyclo(2.2.1)hepta-2,5-diene] and 65 mL of ethyl chloride (Notes 1 and 2). The system is then cooled to -123°C (Note 3). Polymerization is initiated by introducing 14 mL of a solution of aluminum chloride in ethyl chloride at a concentration of 0.19 mol/L (Note 4). The reaction starts immediately upon initiator addition and is marked by the development of haziness. The reaction is terminated after 37 min of stirring at -123°C by introducing precooled n-propanol. The temperature is raised to evaporate the solvent, the precipitated polymer is repeatedly washed with methanol, and the product is dried in vacuo at 60°C for 48 h; yd 1.753 g (17.25%, Note 5).

2. Characterization

The product is an amorphous (by x-ray diffraction) white powder, and is completely soluble in benzene, toluene, ether, and carbon tetrachloride (Note 6). It decomposes before it melts. Its number-average molecular weight by vapor phase osmometry is ca 5500, corresponding to a degree of polymerization of ca 60.

3. Notes

1. Norbornadiene, obtained from Matheson, Coleman, and Bell, 2902 Highland Ave., Norwood, Ohio 45212, was distilled before use. Gas chromatographic analysis indicated better than 98% purity. Ethyl chloride, research grade from Matheson Gas Products, 1275 Valley Brook Ave., Lyndhurst, New Jersey 07071, was passed through tubes filled with porous barium oxide and Linde 4A molecular sieves and was condensed at -78°C in the dry box under nitrogen.
2. Well-cooled pipets are necessary to handle liquefied ethyl chloride. Precooling can be conveniently done by immersing the pipets in a cooled inert liquid (n-pentane).
3. A convenient dry box for carrying out low temperature polymerizations under an inert atmosphere has been described.\(^3\)
4. The initiator solution is prepared by dissolving quantities of purest aluminum chloride in ethyl chloride at -78°, removing the undissolved salt by filtration through fritted glass, and determining the aluminum chloride concentration by titration. A titration method has been published.  
5. The checker obtained high yields, 40-50% using incremental additions of the aluminum chloride solution.  
6. At higher temperatures, such as -100°, a partially cross-linked product is obtained.

4. Methods of Preparation

The preparation of high molecular weight polynortricyclene was first described in 1965 and a convenient laboratory apparatus was reported in detail.

5. References

1. Institute of Polymer Science, University of Akron, Akron, Ohio 44325.  
2. Exxon Research and Engineering Co., P. O. Box 45, Linden, New Jersey 07036.  