Anti-Bredt Monomers

4. Polymerization of 1-Aza-3-Oxabicyclo[3.3.1]Nonan-2-One

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Summary:

1-Aza-3-oxabicyclo[3.3.1]nonan-2-one, an N-bridgehead bicyclic urethane, polymerized in bulk under the influence of dibutyltin oxide and p-toluenesulfonic acid. In solution the monomer polymerizes in the presence of phosphoric acid. This is only the second example of ring opening polymerization of a bicyclo-[3.3.1]nonane. The driving force in the present case is thought to be the relief of strain energy in the monomer conferred by its chair-boat conformation.

Introduction:

A characteristic feature of title compound $3$ is the presence of the bridgehead nitrogen atom, which is a cause of instability since the N-CO resonance interaction is prohibited if the molecule exists in a two-chair form (BREDT, THOUET, and SCHMITZ 1924, LUKES 1939, WISEMAN 1970).
Although the presence of the adjacent oxygen atom partially satisfies the demand of the carbonyl group for electrons, this compound is expected to polymerize to recover full N-CO resonance interaction as well as a strainless chair conformation.

**Instrumentation:**

NMR spectra were obtained using Varian T-60. Infrared spectra were determined on a Perkin-Elmer 337 grating infrared spectrophotometer. Mass spectra were determined on a Hewlett-Packard 5930 A quadrupole mass spectrometer. Elemental analyses were performed by Chemalytics, Inc., Tempe, Arizona or by the University Analytical Center, Department of Chemistry, University of Arizona, Tucson. The number average molecular weight of polymers were determined on dichloroethane solutions at 37°C using Hewlett-Packard Vapor Pressure Osmometer Model 302B. All the melting points were determined in °C in a Thomas-Hoover melting point apparatus and are uncorrected.

**Experimental:**

3-(Hydroxymethyl)piperidinium p-Toluenesulfonate Salt 

3-Piperidinemethanol (bp 72°/0.05 mm, 20.7 mmole, 2.38g) was dissolved in 50 mL absolute ethyl alcohol (warm). An equimolar amount of p-toluenesulfonic acid monohydrate (3.93g) was added. When anhydrous ether was added, a white cloud appeared which condensed into an oil. This oil solidified by cooling at 10° for 3 days and white needle crystals appeared above it. This was filtered and recrystallized from an ethyl acetate ethanol mixture (1:1), mp 76-78°, 54% yield.

CHN analysis as calculated for C_{7}H_{11}NO_{2}:

Calc: C 54.36  H 7.32  N 4.88  S 11.15

Found: 53.32  7.33  4.38  11.42