CATIONIC TRANSANNULAR OLIGOMERIZATION OF 1,5-CYCLOOCTADIENE

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ABSTRACT

Cationic transannular oligomerization of 1,5-cyclooctadiene initiated by BF$_3$OEt$_2$ and AlCl$_3$ is presented in this paper. The number-average molecular weight of the resultant polymer is about 1,500, and the softening temperature range is 140-160°C. By means of NMR, IR and PC-MS analyses, the chain structure of poly(1,5-cyclooctadiene) proposed earlier by Marvel et al. is corroborated.

INTRODUCTION

In 1963, Marvel et al. (1) reported that 1,5-cyclooctadiene (COD), in the presence of triisobutyl-aluminum and titanium tetrachloride yielded an essentially saturated polymer. The authors suggested a mechanism of transannular polymerization. Recently, the authors of this paper carried out the transannular polymerization of 1,5-cyclooctadiene with AlCl$_3$ as a catalyst (2). However, the structure of the oligomer has not been definitely confirmed by experimental data. This work concerns the cationic transannular polymerization of 1,5-cyclooctadiene initiated by BF$_3$OEt$_2$ and AlCl$_3$. The effects of reaction conditions such as the concentrations of the catalyst and the monomer, etc. on the polymer yield are investigated. Spectrographic (PC-MS) studies ascertain that the resulting polymer is poly-2,6-bicyclo-(3,3,0)octane.

EXPERIMENTAL

Materials

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Cis,Cis-1,5-cyclooctadiene was supplied by Aldrich Chemical Company. Prior to polymerization, 1,5-cyclooctadiene was purified by repeated shaking with concentrated sodium hydroxide solution for three times at room temperature, then was washed with dilute sulfuric acid and with water. Predried solvent with calcium hydride was distilled under reduced pressure. Dichloromethane was refluxed over calcium hydride for 24 hr. and distilled under an atmosphere of nitrogen. The water content in COD was determined by means of Karl-Fischer method which should be within 15 ppm, and for one in dichloromethane should be less than 6 ppm.

**Polymerization**

When using such liquid catalyst as BF$_3$OEt$_2$, the polymerization was carried out in dry 20 ml ampoules to which the monomer, the solvent, and the catalyst were added by hypodermic syringes. Then the ampoules were sealed and left alone at the desired temperature. The reaction was terminated by addition of alcohol and hydrochloric acid. The products were dissolved in chloroform, then precipitated, filtered and washed three times with alcohol, and dried to constant weight in vacuo at 40°C. The polymer yield was determined by weighing.

For initiation by AlCl$_3$, the polymerizations were carried out in a dry serum bottle, in which the bulb containing AlCl$_3$ was previously placed. The monomer and the solvent were added through the rubber cap to the serum bottle with hypodermic syringes, and then the bulb can be shattered by means of stirring the bottle, at the same time the reaction began. The termination of reaction and the purification of polymers were the same as those mentioned above.

**RESULTS AND DISCUSSION**

**Effect of the molar ratio of catalyst to monomer on polymer yield**

1,5-cyclooctadiene was polymerized with BF$_3$OEt$_2$ and AlCl$_3$ in CH$_2$Cl$_2$ under fixed reaction conditions. The results are shown in Figures 1 and 2, which indicate that the polymer yield increases with the elevation of the molar ratio of catalyst to monomer, and finally reaches a limited polymer yield.

**Effect of solvent**

It is well known that the rate of cationic polymerization will increase greatly as one increases the solvating power of the reaction medium(3,4).