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Oligomerization of Isocyanates by Cyclic Sulfonium Zwitterions

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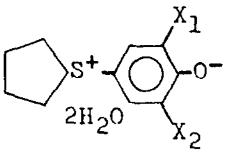
Introduction

The volatility of difunctional isocyanates (such as tolylene diisocyanates, hexamethylene diisocyanate, etc.) createsmany environmental problems in the urethane industry. These difficulties can be overcome by preparation of NCO-terminated oligomers with low vapor pressure. One approach is preparation of NCO-terminated oligomers by partial cyclotrimerization of difunctional isocyanates. Usually this is achieved by a multi-step process which includes also deactivation of the catalyst at a certain conversion. During our work on cyclotrimerization of isocyanates we found that cyclic sulfonium zwitterions are very active cyclotrimerization catalysts (KRESTA, SHEN, 1977, 1978). Recently we found that cyclic sulfonium zwitterions under certain reaction conditions act as anionic initiators. This behavior of cyclic sulfonium zwitterions permits preparation of isocyanate oligomers containing isocyanurate rings by a one-step procedure, eliminating the deactivation step. In this communication this one-step procedure will be discussed.

Results and Discussion

The cyclic sulfonium zwitterions of the general formula



(I)

$X_{1,2}$ = H, R

contain 2 molecules of water. The water forms a protective barrier which prevents interaction between the ions. SCHMIDT and HATCH (1972) found that removal of the water caused a nucleophilic attack of the anion on the tetrahydrothiophenium ring, followed by ring opening and consecutive polymerization:

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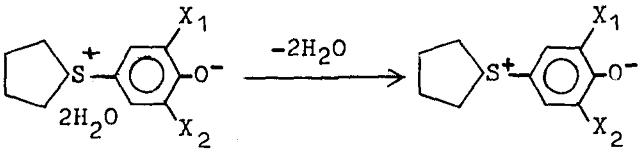
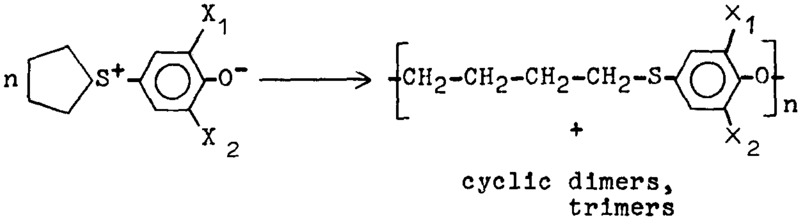
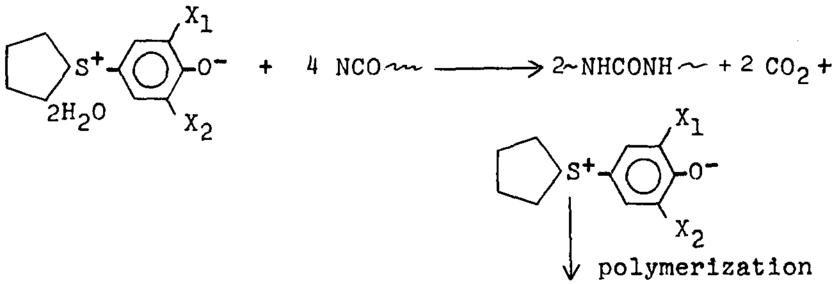




(II)

In diluted aprotic solutions the reaction rate between isocyanates and stabilizing water is negligible but becomes important at high concentrations of isocyanates and high reaction temperatures. This deactivation reaction transfers an active catalyst into the inert (non-reactive) polymer:



(II)

Thus, the final conversion of oligomerization (cyclotrimerization) of isocyanates can be controlled by the amount of catalyst added to the reaction system. The resulting NCO-containing oligomers are stable because the polymer formed from the catalyst does not contain ionic or other catalytically active centers.

Experimental

The NCO-terminated oligomers were prepared by controlled partial cyclotrimerization of 2,4-tolylene diisocyanate (TDI) in butyl acetate. The catalyst used in this study was 2-methyl-4-(1-thiolanylium) phenolate dihydrate (SZ), a product of the Dow Chemical Company. Butyl acetate (BA, from Baker Chem. Co., anal. grade) was dried over potassium carbonate (5 g/l), anhydrous magnesium sulfate (5 g/l) for two days, then distilled. The fraction with a constant boiling point was collected and kept under nitrogen. Acetonitrile (AN, 99.64%, from Vistron Corp.) was refluxed with phosphorus pentoxide (5 g/l), then with calcium hydride (2 g/l) and then distilled under nitrogen. 2,4-TDI was obtained from the Mobay Chem. Co. (99%).

Preparation of the NCO-terminated Oligomer

The preparation was carried out in a dried 250 ml three-necked flask equipped with a nitrogen inlet, magnetic stirrer, reflux condenser, micro-dropping funnel and recording thermocouple. The reaction flask was immersed in a constant temperature bath (25°C) and 100 ml of the 2,4-TDI solution in butyl acetate (50% vol.) were placed into the flask. When a constant temperature was reached in the flask, one ml of a solution of a catalyst in acetonitrile (containing 6 mg of SZ) was added dropwise to the reaction mixture and the resultant mixture was intensively mixed for 4 hours. The reaction product contained 10.9% NCO (63% conv.). The GPC analysis revealed that the reaction product was predominantly tetrafunctional (2 isocyanurate rings) NCO-terminated oligomers. The rate of disappearance of the NCO group during the preparation is presented in Figure 1.

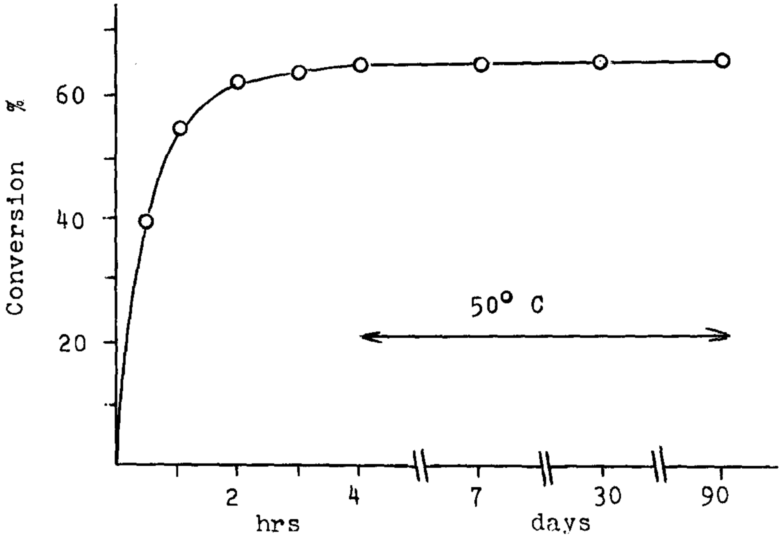


FIG.1.Oligomerization of 2,4 TDI by cyclic sulfonium zwitterions.

Summary

The cyclic sulfonium zwitterions (I) are very effective catalysts for the cyclotrimerization of isocyanates. Under certain conditions (high concentration of isocyanate in the reaction system or high reaction temperature) cyclic sulfonium zwitterions act as anionic initiators. This behavior is due to the reaction of the isocyanate with stabilizing molecules of water of cyclic sulfonium zwitterions followed by rapid polymerization of the initiator. This phenomenon can be easily utilized in the one-step preparation of stable NCO-terminated oligomers of difunctional isocyanates.

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