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Green processes to diisocyanates and polyurethane-urea elastomers via carbonate raw materials: New NPR and NIR processes

Shenghong A Dai, Wen Chen Pan, S J Chen and **Wei Shing Lin**
National Chung-Hsin University, Taiwan

A general non-phosgene route (NPR) of making aromatic as well as aliphatic diisocyanates have been developed through synthesis and then thermolysis of diphenyl N,N'-alkenylbiscarbamates (diphenylbiscarbamates). Diphenylbiscarbamates were prepared readily by carbonylation of diamines with diphenyl carbonate (DPC) under mild condition. Pure aliphatic diphenylbiscarbamates could be isolated in greater than 90% in absence of catalyst, but the aromatic carbamate needed excess of DPC with an amine-salt catalyst. Thermolysis of diphenylbiscarbamates in selective solvents at 240~255^{0}C successfully cracked them into diisocyanates with phenol recovery. Among the study, 1,12-dodecane diisocyanate (DDI, C12-diisocyanate) gives the highest isolation yields of 84%. The yield of MDI, HDI, BDI and 4-IBPI are slightly lower (~70-80%). We also have succeeded in developing a one-pot two-stage NPR process by making the biscarbamate first followed immediately by thermolysis in the same solution. Excellent yield (80%) of diisocyanates was isolated in the one-pot synthesis. It has also been utilized diphenylbiscarbamates synthesized as raw materials to make new segmented polyurea elastomer (PUaE) of high molecular weight through trans-esterification in tetramethylenesulfone (TMS) at moderate tempertues. The key to this NIR process lies in the timing and sequence of the diamine additions. The most optimized polyurea made in this study has thenη_{inh} of 0.64, tensile strength of greater than 30 MPa and elongation exceeding 400% with thermal stability higher than 260~300^{0}C. In the meantime, phenol and TMS can be isolated to facilitate total re-cycling of the substances. Both NIR and NPR processes developed thereby complies fully with the principles of green chemistry.

Biography

Shenghong A Dai completed his PhD at University of Florida and postdoctoral studies at Cornell University, both in Department of Chemistry. He worked as a research chemist at Upjohn (1973-1985) and Dow Chemical USA (1985-1998), before becoming a professor at current NCHU (1998-now) in Taiwan. He has published more than 70 papers in reputed journals with more than 50 patents applications.

shdai@dragon.nchu.edu.tw