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13. ABSTRACT (Maximum 200 words) The synthesis and polymerization of a wide variety of azaethylenes (imines) and azabutadiene were studied. The overall results were modest. Despite systematic manipulation of substituents to favor polymerization, high polymers were obtained infrequently and their physical properties were not outstanding. Exploratory work led to novel polyaromatic quinonimines. This led to an AASERT project where this work will be described in detail.				
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**SYNTHESIS AND POLYMERIZATION OF NEW IMINE MONOMERS:
AZAETHYLENES, AZABUTADIENES, AND AZAALLENES**

FINAL PROGRESS REPORT

H.K. HALL, JR.

JUNE 18, 1996

U.S. ARMY RESEARCH OFFICE

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STATEMENT OF THE PROBLEMS STUDIED

AND

A SUMMARY OF THE MOST IMPORTANT RESULTS

Summary

Synthesis and Polymerization of Imines (Azaethylenes and Azabutadienes)

Statement of the Problem - In polymer chemistry the polymerization of olefins ($C=C$) and carbonyl monomers ($C=O$) is well established. In contrast, very little monomer-polymer chemistry is known for imines ($C=N$). A fundamental study of this problem was undertaken. Our approach was to synthesize new $C=N$ monomers. The requirements were that these be isolable and purifiable, yet reactive in addition polymerizations and copolymerizations. Substituents would be kept to a minimum but stabilizing substituents on nitrogen would facilitate anionic radical or cationic polymerization. Our earlier work on the imines and azadienes was reviewed in Makromolekulare Chemie Symposium. [H.K. Hall, Jr. "Synthesis and Polymerization of Imines and Azadienes: New Polymerizable Monomers" Makromol. Chem., Macromol Symp. 54/55, 73 (1992)]" The general indications at that stage was that simple imines were a very limited class of monomers but that the 1-azadienes was a satisfactory new class. More recently we were able to detect C,N-dicyanomethane imine as an exceptionally reactive and fugitive monomer whose presence could be established only by trapping. A family of C-arylimines with several electron-accepting substituents on nitrogen was synthesized. Their attempted polymerizations led only to oligomers. Formaldehyde oxime and its o-benzyl derivatives were examined, but again only low molecular weights were obtained in this case by cationic polymerization. Here cyclic trimer was the product found most often.

As to the azadienes, 3-methyl-N-phenylsulfonyl 1-aza-1,3-butadiene oligomerized anionically and participated in free radical copolymerizations with styrene comonomers. Studies aimed at synthesizing and polymerizing N-cyano-1-azabutadienes proved to be difficult and no real polymers could be obtained.

Summing up all of the above work, it appears that our goal of identifying useful readily available and polymerizable imine monomers has not been met. In general, the monomers are difficult to purify, hydrolytically unstable and do not polymerize high molecular weight materials.

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