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POLYMERIZATION OF AZAETHYLENES (IMINES) AND
AZA-13-DIENES POTENTIAL REACTIVE MONOMERS(U) ARIZONA
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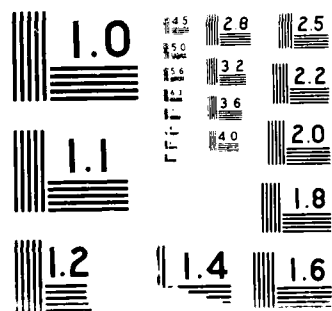
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Polymerization of Azæthylenes (Imines) and
Aza-1,3-dienes. Potential Reactive Monomers.

FINAL REPORT

H. K. Hall, Jr.

April 1, 1988

U.S. Army Research Office

Grant DAAG29-85-K-0068

University of Arizona

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Statement of Problem

Although a great deal of chemistry is known about the polymerization of C=C and C=O compounds, very little is known about the polymerization of C=N compounds. The literature does contain tantalizing hints of the ability of azaethylenes (imines) to polymerize. Thus, N-alkylazaethylenes are known to cyclotrimerize. However, before our work, no systematic study has been carried out.

We shall call imines "azaethylenes" to point out their relationship to vinyl monomers. The aza-1,3-dienes are then equivalents of butadienes.

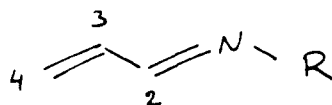
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Results

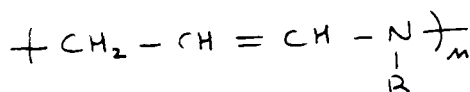
Several types of new imine monomers have been synthesized and their polymerizability has then been investigated in different conditions. The main classes of imines studied include 1-aza-1,3-butadienes with an electron donating or electron-accepting substituent on nitrogen, 2-aza-1,3-butadienes with a substituent in the 1-position, imines with three electron-accepting. Substituents, and imines with only one electron-accepting substituent.

1-Azabutadienes

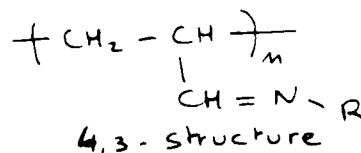
We began our work with a study of the synthesis and polymerization of 1-azabutadienes:



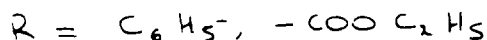
We synthesized various 1-substituted 1-azabutadienes via pyrolysis of cyclopentadiene adducts. We found that the substituent on N and the type of initiator played major roles in bringing about 4,1 polymerization of 1-azabutadienes. Donor groups on N such as $\text{CH}_3\text{O}-$, $(\text{CH}_3)_2\text{N}^-$, C_6H_5^- with electrophilic initiators did not give cationic polymerization, but only stable ammonium salts. But acceptor groups (C_6H_5- , $-\text{COOC}_2\text{H}_5$) with anionic initiators gave high yields of high polymer with 4,1 structure (2).



4,1-structure



4,3-structure

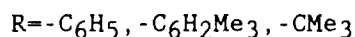


With free radical initiators, 1-azabutadienes with donor or acceptor groups on nitrogen gave indifferent results. One problem we encountered was

that N-carboethoxy-1-azabutadiene tends to dimerize in these conditions (70°). This unwanted hetero-Diels-Alder reaction of the C=N-C=O unit effectively competes with the radical polymerization. (The anionic polymerization mentioned above proceeds faster at lower temperature.) We had earlier demonstrated this ability of a -COOR acceptor group in conjugation with C=N group to undergo hetero-Diels-Alder for triethyl ethyleneiminetricarboxylate.

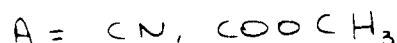
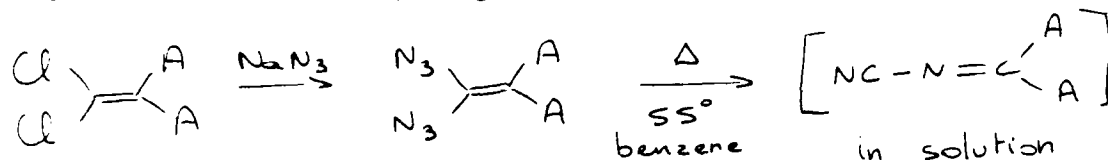
2-Azabutadienes

Several 1-substituted-2-azabutadienes have also been synthesized via pyrolysis. The substituents were phenyl, 2,4,6-trimethylphenyl and t-butyl. Only the first one led to low molecular weight polymer. Thus, we showed that polymerization involving propagation in the sense $\sim * + N=C \longrightarrow \sim N-C*$, where * = +, ., or - is not suitable.

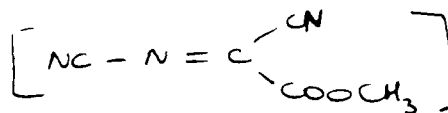
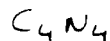
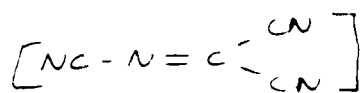


Azaethylenes (Imines)

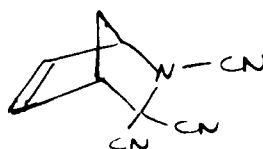
We have devised, based on literature suggestions, a new synthesis of azaethylenes with three acceptor groups.



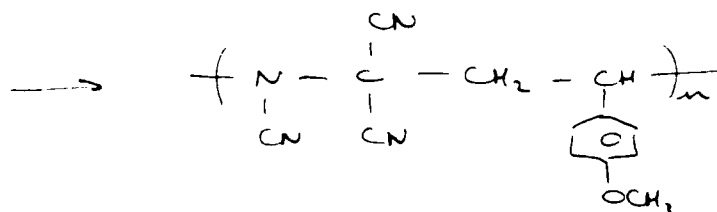
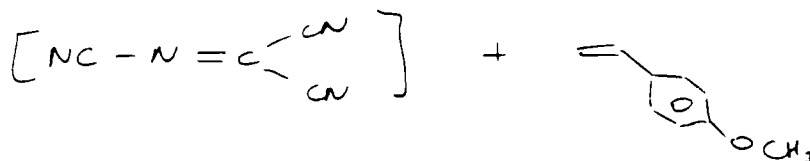
So far, we have studied:



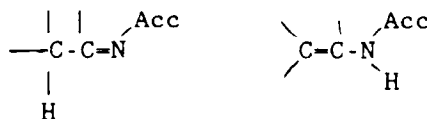
The C_4N_4 is very reactive. Attempted isolation gives only oligomeric material, even when acidic stabilizers or freeze-drying are employed. The cyanoester monomer is more stable in solution and its spectra can be obtained. Thus, ester groups instead of cyano groups on carbon offer somewhat lower reactivity and hope of isolation and purification. Nevertheless, again isolation does not succeed. Conclusive evidence for the presence of both of these highly reactive azaethylene monomers was obtained by trapping them as Diels-Alder cycloadducts with cyclopentadiene:



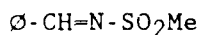
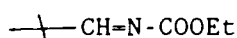
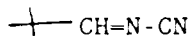
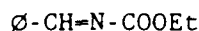
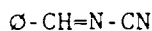
Upon mixing with p-methoxystyrene, these two highly electrophilic azaethylenes spontaneously formed strictly alternating copolymers.



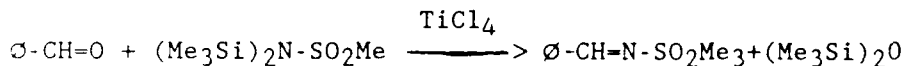
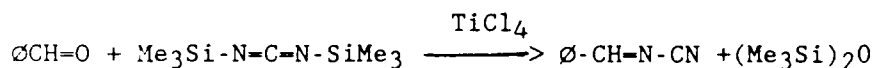
Turning to less reactive imines, we turned to azaethylenes with only an electron-accepting substituent on N. In order to avoid tautomerization to enimides, the substituents on carbon should not have any β -hydrogens.



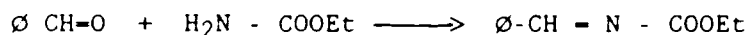
The following imines were selected:



The N-cyano and N-sulfonyl imines were synthesized using silylated reagents. For example.



The N-carboethoxy imines were synthesized by reaction of the aldehyde with ethyl carbonate:



The N-cyanoimines both polymerized in high yield under anionic or free radical conditions, but molecular weights were low. The other three imines did not polymerize. The low steric requirement of =N-CN (linear) versus = N-COOEt or = N - SO₂Me appears responsible.

Conclusions

To sum up our USARO work, we have made great progress in understanding how to design and polymerize azaethylene monomers:

1. We have designed new general synthesis of N-acceptor-azaethylene monomers.
2. Suitable acceptor groups on N include CN and COOR.
3. Two acceptor groups on carbon have led to too reactive monomers, although they can be detected in solution, and monomers with less powerful acceptor groups may still be isolable.
4. Donor substituents on carbon should be aryl or t-butyl. Alkyls with β -H are unsuitable because of tautomerization. Two hydrogens will lead to too reactive monomers.
5. Anionic and free radical polymerization are the methods of choice.
6. The C=N-Acc monomers and polymerization resemble the anionic polymerization of aldehydes.

The polymers obtained so far have been white solids with T_g 50-125°, in general, soluble in organic solvents, and suitable for binder materials.

Publications under USARO Sponsorship

1. T. Kitayama and H.K. Hall, Jr., "Synthesis and Polymerization of 1-Azabutadiene Monomers," Macromolecules, 20, 1451 (1987).
2. J. Oku, A.B. Padias, H.K. Hall, Jr. and A.J. East, "Poly (3-Butyl-3-ethyl Malonimide)," Macromolecules, 20, 2314 (1987).
3. T. Kitayama, A.B. Padias, and H.K. Hall, Jr., "On the Polymerization of 1-substituted 1-Aza-1,3-butadienes," Polym. Bull., 17, 417 (1987).
4. M. Ramezani, F.D. Saeva and H.K. Hall, Jr., "A New Azacyanocarbon, C_4N_4 : Tricyanomethanimine," Tetrah. Lett. (in press).
5. J.B. Kim and H.K. Hall, Jr. "Synthesis and Polymerization of 1-Carboethoxy-3-methyl-1-aza-1,3-butadiene," Macromolecules (in press).

6. J.B. Kim, A.B. Padias and H.K. Hall, Jr., "Synthesis and Polymerization of Electron-Deficient Imines," (in preparation).
7. M. Ramezani and H.K. Hall, Jr., "Synthesis and Polymerization of N-Cyanoimines", (in preparation).

Scientific Personnel

H.K. Hall, Jr.	Principal Investigator, 3 summer months
T. Kitayama	Postdoctoral, 1 year
J. B. Kim	Postdoctoral, 1 year
J. I. Oku	Postdoctoral, 6 months
J. I. Weinschenk	Graduate Student, 6 months
M. Ramezani	Graduate Student, 18 months

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