NASA CR-100681

YEARLY SUMMARY REPORT

TO THE

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

ON THE

SYNTHESIS OF POLYMERS WITH HIGH RESIDUES AT HIGH TEMPERATURES

PERFORMED

UNDER

NASA GRANT NGR-15-004-028

February 1969

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF NOTRE DAME
NOTRE DAME, INDIANA 46556

FOREWORD

This report summarizes activities under this grant for the period February 1, 1968 to January 31, 1969.

The research under NASA Grant NGR-15-004-028 is being conducted in the Department of Chemistry, University of Notre Dame, Notre Dame, Indiana 46556, under the technical direction of Professor G. F. D'Alelio, principal investigator.

This report covers activities performed by G. F. D'Alelio and R. K. Mehta assigned to the Project. In addition, W. F. Strazik, H. E. Kieffer, D. M. Feigl, and R. L. Germonprez, not officially assigned to the project, voluntarily contributed research time and effort.

The technical aspect of this grant is monitored by Dr. John A. Parker, NASA-Ames Laboratory, Moffett Field, California 94035.

Date February 15, 1969

Signed G F D'Alelio

G. F. D'Alelio
Principal Investigator

ACTIVITIES UNDER NGR-15-004-028

I. Publications.

The researches reported in the following papers were supported in part by this grant and in part by NASA Grant NsG339.

A. Polymeric Schiff Bases. XIII. The Direct Synthesis of Crosslinked Polymeric Azomethines, by G.F. D'Alelio, D.M. Feigl, H.E. Kieffer, and R.K. Mehta. J. Macromol Sci.-Chem., A2(6), 1223-1234 (1968). (In press).

B. Polymeric Schiff Bases. XIV. The Synthesis of Crosslinked Polymeric Azomethines by Exchange Reaction, by G.F. D'Alelio, R.K. Mehta, D.M. Feigl, H.E. Kieffer, and R.L. Germonprez. J. Macromol. Sci.-Chem., A2(6), 1235-1259 (1968). (In press).

C. Polymeric Schiff Bases. XV. The Synthesis of Crosslinked Polymeric Azomethines from Aminoarylketones, by G.F. D'Alelio, H.E. Kieffer, R.L. Germonprez and R.K. Mehta. J. Macromol. Sci.-Chem., A2(6), 1261-1269 (1968). (In press).

D. Polymeric Schiff Bases. XVI. Alternate Syntheses for the Iminobenzylidene Polymers, by G.F. D'Alelio, F.R. Meyers, W.F. Strazik, and R.L. Germonprez. J. Macromol. Sci.-Chem., A2(7), 1333-1351 (1968). (In press).

E. Polymeric Schiff Bases. XVII. Azomethine Copolymers, by G.F. D'Alelio, W.F. Strazik, D.M. Feigl, and R.K. Schoenig. J. Macromol. Sci.-Chem., A2(8) 1457-1490 (1968). (In press).

F. Structural Design and Thermal Properties of Polymers. G.F. D'Alelio. Invited Lecture presented at the "Symposium on Ablative Plastics," National Meeting of the American Chemical Society, San Francisco, California, April 1-5, 1968.

G. Ablative Plastics, co-edited with J.A. Parker, Ames Laboratory-NASA. Volume contains the twenty-one papers presented at the symposium (See F.). (In press; J. Macromol. Sci., Symposium Volume).

H. The Synthesis of Thermally Stable Polymeric Azomethines by Polycondensation Reactions. G.F. D'Alelio and R.K. Schoenig. Presented at the "Symposium on Polycondensation" at the National Meeting of the American Chemical Society, San Francisco, California, April 1-5, 1968.

I. The Synthesis of Thermally Stable Polymeric Azomethines by Polycondensation Reactions, by G.F. D'Alelio and R.K. Schoenig. (In press, J. Macromol. Sci.-Reviews in Macromolecular Chemistry).

J. Polyazomethines. G. F. D'Alelio. In press, Encyclopedia of Polymer Science and Technology.

K. The Direct Synthesis of Crosslinked Polymeric Azomethines, by G.F. D'Alelio, D.M. Feigl, H.E. Kieffer and R.K. Mehta. Presented at Symposium on "Polymers in Space Research" held under the auspices of the Southern California Section of the American Chemical Society, Jet Propulsion Laboratory, California Institute of Technology, July 15-17, 1968. Symposium papers are expected to be published in the Journal of Macromolecular Science-Symposia.

Preprints of these papers were forwarded to the Office of University Affairs, Code Y, National Aeronautics and Space Administration, Washington, D.C. 20546, and to Dr. John A. Parker, NASA-Ames Research Center, Moffett Field, California 94035. The results in papers XIII, XIV, XV and XVII may be patentable.

II. Status of Other Research Activities.

A. Polymeric Schiff Bases. XVIII. Novel Polymerization Reactions of Azomethines. G.F. D'Alelio and R.K. Mehta.

This activity was supported solely by Grant NGR-15-004-028. Studies were undertaken to explain the origin of by-product aniline in bis-Schiff-base exchange polymerizations, such as are reported in the papers: Polymeric Schiff Bases XIII, XIV and XV. Polymeric Schiff bases prepared by direct condensation yield little or no aniline as a by-product. Since the major difference between the two types of reaction is the presence of by-product benzylideneaniline found only in the bis-exchange reactions, it was speculated that benzylideneaniline originated the aniline either by self-condensation or by condensation with the Schiff-base structures available in polymer present in the reaction mixture. To evaluate this speculation, a wide variety of mono-functional, di-functional and tri-functional Schiff bases were heated in an inert atmosphere in the absence of added catalysts or in the presence of various amounts of zinc chloride as a mild Lewis acid catalyst, following which the products of the thermal treatment were isolated, and, to a large degree, identified or characterized. This study was particularly productive and led to the discovery of some new reactions of Schiff bases, and that, many simple Schiff bases, such as $C_6H_5N{=}HCC_6H_4CH{=}NC_6H_5$, $C_6H_5CH{=}NC_6H_4N{=}CHC_6H_5$, etc., can be polymerized alone to yield aniline as a by-product and a thermally stable polymer which has a polystilbene character. These studies have been completed and the data have been assembled for organization into a publication. The first draft of introduction and experimental sections of the projected paper is completed. The assembly of the results into about twelve or more tables is in progress, following which, the discussion section will be written. When completed, preprints will be submitted to NASA, as required, at the same time the paper is submitted to the Journal for consideration for publication. The results of this study appear to be patentable.

B. Crosslinked Polyimides.

The thermally stable polyimides are derived from aromatic tetracarboxylic acids and aromatic diamines. The structure of these polymers is normally written as linear; undoubtedly when these polymers are heated to high temperatures crosslinking occurs either through transamidation or radical formation, etc. Since crosslinking usually improves the thermal stability of linear polymers, a study was undertaken to synthesize polyimides that contained deliberately introduced crosslinks. Two approaches were investigated. One approach visualized the use of crosslinking amines, while the other approach considered triimide-forming polycarboxylic acids.

The effort on this study has been minimal; it was kept active by utilizing spare time whenever it became available under activity II.A Thus, the studies were exploratory only.

1. Modification of Polyimides by 1,3,5-$C_6H_3(NH_2)_3$.

The 1,3,5-triaminobenzene (TAB) is a particularly oxygen-sensitive material which is prepared by the catalytic reduction of 1,3,5-trinitrobenzene. A number of polycondensations were performed in dimethylacetamide using pyromellitic anhydride (PMA), m-phenylenediamine (PDA) and various amounts of the triaminobenzene substituted for an equivalent amount of the phenylenediamine replaced. The exploratory experiments indicated that the two moles of TAB cannot be condensed with three moles of PMA because premature crosslinking and gellation or precipitation occurred. However, TAB can be used to modify the reaction of PMA with PDA without premature gellation in amounts equivalent to sixty mole percent of the PDA; the NH_2 molar equivalency of TAB to PDA is 2 $C_6H_3(NH_2)_2$: 3 $C_6H_4(NH_2)_2$.

2. Modification of Polyimides by $C_6[(CO)_2O]_3$.

In contrast to 1,3,5-triaminobenzene, mellitic trianhydride is not oxygen-sensitive, is more easily handled and processed and would serve the same purpose of introducing crosslinks in the polymer.

Exploratory experiments in dimethylacetamide paralleling those under B.1 above were performed. In this case, the trimellitic anhydride was substituted for equivalent amounts of pyromellitic anhydride. The exploratory experiments yielded surprising results. It was found possible to prepare polymers soluble in dimethylacetamide used as the solvent for the reaction, in which any equivalent amount or all of the pyromellitic anhydride had been replaced by mellitic trianhydride.

The advantages of mellitic trianhydride, as a crosslinking agent for the polyimides, are so markedly higher than triaminobenzene, that future efforts will be devoted to it first. However, if time permits, studies using the triamine will be reinitiated and different procedures will be evaluated in the triamine system. For example, non-stoichiometric systems of pyromellitic anhydride and diamines will be condensed first, then the triamine will be added at some late stage of condensation, experimentally determined, which, hopefully will allow the polymer to stay in solution. If successful, crosslinking then can be achieved after the solvent is eliminated.