②

NASA
Technical Memorandum 102353

AVSCOM
Technical Report 89-C-017

3F Condensation Polyimides—Review and Update

William B. Alston
Propulsion Directorate
U.S. Army Aviation Research and Technology Activity—AVSCOM
Lewis Research Center
Cleveland, Ohio

and

Roy F. Gratz
Mary Washington College
Fredericksburg, Virginia

Prepared for the
First Pacific Polymer Conference
sponsored by the Pacific Polymer Federation, Inc.
Lahaina, Maui, Hawaii, December 12-15, 1989

NASA

US ARMY
AVIATION
SYSTEMS COMMAND
AVIATION R&T ACTIVITY

3F CONDENSATION POLYIMIDES - REVIEW AND UPDATE

William B. Alston
Propulsion Directorate
U.S. Army Aviation Research and Technology Activity - AVSCOM
Lewis Research Center
Cleveland, Ohio 44135

and

Roy F. Gratz
Department of Chemistry and Geology
Mary Washington College
Fredericksburg, Virginia 22401

The presence of the hexafluoroisopropylidene (6F) connecting group in aryl dianhydrides used to prepare aromatic polyimides provides high glass transition temperature (T_g) polyimides that exhibit high thermo-oxidative stability (TOS) and good processability as matrix resins ~~(~~ref. 1). The overall objective of this study was to determine if a phenyltrifluoroethylidene (1-phenyl-2,2,2-trifluoroethane, 3F) connecting group would have a similar effect as a 6F group on the processability, T_g and TOS of aromatic polyimides. A new dianhydride containing the 3F connecting group was synthesized. This new 3F dianhydride (3FDA) and 3F diamine (3FDAM, ~~refs. 2 to 4~~) were polymerized together and also with other diamines or dianhydrides to prepare new polyimides. The new 3F containing polyimides and analogous 6F polyimides were prepared by condensation polymerization via traditional amic-acid polymerizations in N,N-dimethylacetamide (DMAc). The amic-acid solutions, with two exceptions, had inherent viscosities greater than 0.45 dl/g, indicating that high molecular weight polymers had been formed. Structure-to-property relationships correlating inherent viscosity to the basicity of those diamine monomers which contained 3F and 6F connecting linkages were observed and explained in a prior report ~~(ref.~~ 4).

The amic-acid solutions were cast as films and then thermally converted into polyimide films at 300 to 500 °C, usually 350 °C, in a nitrogen atmosphere. These films were then pulverized into molding powders and processed into neat resin disks at temperatures and pressures as high as 468 °C/34.5 MPa. Additional resin disks were processed with similar conditions from some 3FDA or 3FDAM molding powders prepared using other techniques as described in reference 4. These techniques included precipitation of the amic-acid molding powders from DMAc solutions, thermal or chemical imidization of the dried precipitated amic-acid powders, and preparation from stoichiometric amounts of diamine and diacid-diester monomer mixtures.

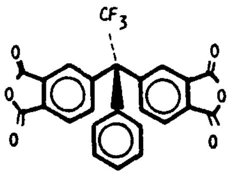
The T_g's of the films and resin disks were determined by thermomechanical analysis (TMA) and were the subject of a prior report (ref. 4) which identified two new polyimides of $T_g \geq 371$ °C (3FDA/paraphenylene diamine (PPDA), $T_g \cong 370$ °C, and pyromellitic dianhydride (PMDA)/3FDAM, $T_g \cong 440$ °C). The thermal stability and TOS of these 3F polyimide films and the analogous 6F polyimide films were determined by thermogravimetric analysis (TGA). The isothermal weight losses of the films and the resin disks at 316 °C, 371 °C, and also at 371 °C under 0.5 MPa (~5 atm) air pressure were determined (using a

E-5062

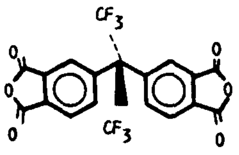
weight loss per unit surface area basis). The results of these studies identified two new 3F containing polyimides (3FDA/PPDA and 6F dianhydride (6FDA)/3FDAM) that exhibit low rates of weight loss comparable to the 6FDA/PPDA and PMDA/6F diamine (6FDAM) resins known to have superior TOS. The study also showed that the resin disks exhibited the same overall trends in weight loss per unit surface area as their respective films, however, the weight loss per unit surface area of the disks was about an order of magnitude greater. This was presumably due to some mechanical degradation induced during the grinding of the molding powders and/or a greater internal (thus, unmeasured) surface area in the resin disks compared to the films. These overall results indicate that polyimides containing the 3F linkage exhibit thermal stability and TOS comparable to polyimides containing the 6F linkage. These TOS results, together with the prior T_g results (ref. 4), showed that further development of the 3F technology in 3FDA and 3FDAM monomers to produce high T_g polyimides with excellent TOS suitable for 371 °C resin and composite applications continued to be warranted.

Thus, since the last presentation on 3F polyimides (ref. 5) additional monomer work has been done on improving the synthesis of 3FDA by use of a proprietary air oxidation process on the 3F tetramethyl precursor and on making the 3F diamine commercially available (from DAYCHEM Labs, Inc. 1600 N. Broad St., Fairborn, Ohio 45324). In addition, the synthesis of two new di and tetraalkyl substituted 3F diamine monomers was recently reported (ref. 6) under a NASA grant (ref. 7). These two new polyalkyl substituted 3F diamines were polymerized with benzophenone tetracarboxylic dianhydride (BTDA) and PMDA (ref. 6 to 8). The dialkyl substituted 3F polymers had greater inherent viscosities than the tetraalkyl substituted 3F polymers (ref. 6), thus only the dialkyl substituted 3F diamine was polymerized with 6FDA in the subsequent study (ref. 8). The three new dialkyl substituted 3F polyimide films were characterized for TOS by TGA and T_g by TMA before and after a 2 hr exposure to 350 nanometer ultraviolet (UV) light. No changes in the TOS and T_g were observed after the UV exposure, however, the T_g of the UV exposed dialkyl 3F films could be increased dramatically by continued thermal treatment while the unexposed dialkyl 3F films did not exhibit a further advance in T_g after continued thermal treatment. This behavior suggests that the alkyl substituted 3F polyimide films are potential photoresists analogous to the commercially available photoimagable BTDA polymers made with nonfluorinated di and tetraalkyl substituted diamines (ref. 9).

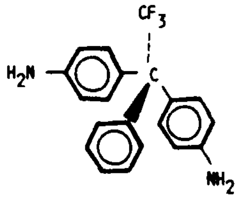
Last, since the prior presentation on 3F polyimides (ref. 5), United States Patents have issued on the new 3F monomer chemistry (refs. 10 and 11) and on new 3F polyimides and 3F composites (refs. 12 to 14). Also, additional United States Patents are pending covering alternative embodiments claimed (ref. 11) within the 3F monomer chemistry investigated.



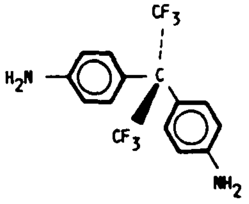
3F DIANHYDRIDE, 3FDA



6F DIANHYDRIDE, 6FDA



3F DIAMINE, 3FDAM



6F DIAMINE, 6FDAM

REFERENCES

1. Gibbs, H.H.: Long-Term Thermal-Oxidative Stability of High Performance Composites Based on Melt Fusible Polyimides. J. Appl. Polym. Sci., Appl. Polym. Symp., vol. 35, 1979, pp. 207-222.

2. Kray, W.D.; and Rosser, R.W.: Synthesis of Multifunctional Triarylfluoroethanes. 1. Condensation of Fluoroketones. J. Org. Chem., vol. 42, no. 7, 1977, pp. 1186-1189.

3. Alston, W.B.: Replacement of MDA With More Oxidatively Stable Diamines in PMR-Polyimides. High Temperature Polymer Matrix Composites, NASA CP-2385, 1985, pp. 187-205 (Also, U.S. Army AVSCOM-TR-85-C-7).

4. Alston, W.B.; and Gratz, R.F.: Structure-to-Glass Transition Temperature Relationships in High Temperature Stable Condensation Polyimides. Recent Advances in Polyimide Science and Technology, W.D. Weber and M.R. Gupta, eds., Society of Plastics Engineers, Poughkeepsie, NY, 1987, pp. 1-15 (Also, NASA TM-87113, U.S. Army AVSCOM-TR-85-C-18).

5. Alston, W.B.; and Gratz, R.F.: Thermo-Oxidatively Stable Condensation Polyimides Containing 1,1,1-Triaryl-2,2,2-Trifluoroethane Dianhydride and Diamine Monomers. Symposium on Recent Advances in Polyimides and Other High Performance Polymers, American Chemical Society, Reno, NV, July 13-16, 1987 (Also, NASA TM-89875 and U.S. Army AVSCOM-TR-87-C-7).

6. McGrady, K.A.; and Gratz, R.F.: New Diamine Monomers for Condensation Polyimides. Virginia Journal of Science, vol. 39, no. 2, 1988, p. 140.

7. Gratz, R.F.: Synthesis of New Diamine and Dianhydride Monomers for Thermooxidatively Stable Polyimides. NASA Grant Number NAG3-794, June 1, 1987 - Present.

8. Crews, M.L.; and Gratz, R.F.: New Condensation Polyimides Containing a Phenyltrifluoroethylidene Linkage. Virginia Journal of Science, vol. 40, no. 2, 1989, to be published.

9. Pfeifer, J.; and Rohde, O.: Direct Photoimaging of Fully Imidized Solvent-Soluble Polyimides. Recent Advances in Polyimide Science and Technology, W.D. Weber and M.R. Gupta, eds., Society of Plastics Engineers, Poughkeepsie, NY, 1987, pp. 336-350.

10. Alston, W.B.; and Gratz, R.F.: Substituted 1,1,1-Triaryl-2,2,2-Trifluoroethanes and Processes for Their Synthesis. U.S. Patent 4,758,380, July 19, 1988.

11. Alston, W.B.; and Gratz, R.F.: Substituted 1,1,1-Triaryl-2,2,2-Trifluoroethanes and Processes for Their Synthesis - Synthetic Routes to Monomers for Polyimides. U.S. Patent Application 924,474, Oct. 29, 1986, (partially allowed for U.S. Patent May 1989).

12. Alston, W.B.; and Gratz, R.F.: Condensation Polyimides Containing 1,1,1-Triaryl-2,2,2-Trifluoroethane Structures. U.S. Patent 4,845,167, July 4, 1989.

13. Scola, D.A.: High Temperature Fluorinated Polyimides. U.S. Patent 4,742,152, May 3, 1988.

14. Scola, D.A.: High Temperature Fluorinated Polymer. U.S. Patent 4,801,682, Jan. 31, 1989.

NASA
National Aeronautics and
Space Administration

Report Documentation Page

1. Report No. NASA TM-102353
AVSCOM TR 89-C-017

2. Government Accession No.

3. Recipient's Catalog No.

4. Title and Subtitle
3F Condensation Polyimides-Review and Update

5. Report Date

6. Performing Organization Code

7. Author(s)
William B. Alston and Roy F. Gratz

8. Performing Organization Report No.
E-5062

10. Work Unit No.
510-01-0A

9. Performing Organization Name and Address
NASA Lewis Research Center
Cleveland, Ohio 44135-3191
and
Propulsion Directorate
U.S. Army Aviation Research and Technology Activity—AVSCOM
Cleveland, Ohio 44135-3127

11. Contract or Grant No.

12. Sponsoring Agency Name and Address
National Aeronautics and Space Administration
Washington, D.C. 20546-0001
and
U.S. Army Aviation Systems Command
St. Louis, Mo. 63120-1798

13. Type of Report and Period Covered
Technical Memorandum

14. Sponsoring Agency Code

15. Supplementary Notes

Prepared for the First Pacific Polymer Conference, sponsored by the Pacific Polymer Federation, Inc. Lahaina, Maui, Hawaii, December 12-15, 1989. William B. Alston, Propulsion Directorate, U.S. Army Aviation Research and Technology Activity—AVSCOM; Roy F. Gratz, Dept. of Chemistry and Geology, Mary Washington College, Fredericksburg, Virginia 22401.

16. Abstract

Nine new condensation polyimides containing the phenyltrifluoroethylidene (3F) linkage were synthesized by the amic-acid route. Several other polyimides, including some with the hexafluoroisopropylidene (6F) linkage, were also prepared as controls. Amic-acid solutions were characterized by determining their inherent viscosities prior to thermal conversion into polyimide films. Glass transition temperatures (T_g), thermogravimetric analysis (TGA), and isothermal weight loss data (at 316, 371, and 371 °C under 0.5 MPa air pressure) were obtained for the films. The films were pulverized into molding powders which, in turn, were thermally processed under pressure into neat resin disks. The disks were also characterized by T_g's and 316 and 371 °C isothermal weight losses. The film study identified two new polyimides with T_g's greater than 371 °C and two new polyimides with low rates of weight loss. The resin disks exhibited the same overall trends in T_g and weight loss as the respective films, however the weight loss per unit surface area was always greater, presumably due to molecular degradation induced during preparation of the molding powders. The overall results indicate that polyimides containing the 3F linkage have T_g's and thermo-oxidative stability comparable to polyimides containing the 6F group. Alternate technology was also shown by the synthesis of two new polyalkyl substituted 3F diamines and five more new 3F polymers. Their potential as photoresists was demonstrated by T_g advancement after ultraviolet exposure. Last, four U.S. patents on 3F monomers and polymers have been issued and up to eight more are pending.

17. Key Words (Suggested by Author(s))
Polyimides; Condensation polymers; High temperature stability; Glass transition temperature (T_g); Thermally and thermo-oxidatively stable; Photoresist polymers

18. Distribution Statement
Unclassified – Unlimited
Subject Category 27

19. Security Classif. (of this report)	20. Security Classif. (of this page)	21. No of pages	22. Price*
Unclassified	Unclassified	5	A01

NASA FORM 1626 OCT 86

*For sale by the National Technical Information Service, Springfield, Virginia 22161