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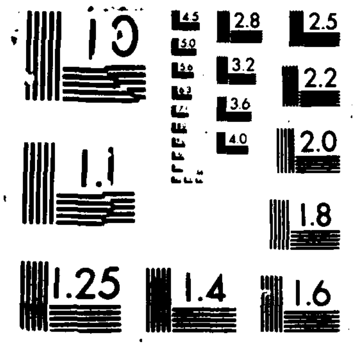
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Thermo-Oxidatively Stable Condensation Polyimides Containing 1,1,1-Triaryl-2,2,2-Trifluoroethane Dianhydride and Diamine Monomers

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THERMO-OXIDATIVELY STABLE CONDENSATION POLYIMIDES CONTAINING 1,1,1-TRIARYL-2,2,2-TRIFLUOROETHANE DIANHYDRIDE AND DIAMINE MONOMERS

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SUMMARY

The presence of the hexafluoroisopropylidene (6F) connecting group in aryl dianhydrides used to prepare aromatic polyimides provides high glass transition temperature (Tg) polyimides that exhibit excellent thermo-oxidative stability. The purpose of this study was to determine if a trifluorophenylethylidene (1-phenyl-2,2,2-trifluoroethane, 3F) connecting group would have a similar effect as a 6F group on the thermo-oxidative stability of aromatic polyimides. A new dianhydride containing the 3F connecting group was synthesized. This new 3F dianhydride and a previously reported (refs. 1 to 3) aromatic diamine also containing the 3F connecting group were used together and in various combinations with known diamines or known dianhydrides, respectively, to prepare new condensation polyimides which contained the 3F group in one or both of the monomers comprising the polymer repeat unit. Known polyimides, including some with the 6F connecting linkage, were also prepared for comparison purposes. The new 3F containing polymers and the analogous comparison 6F polymers were prepared by condensation polymerization via the traditional amic-acid polymerization method in N,N-dimethylacetamide (DMAc) solvent. 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. 3). The solutions were cast as amic-acid films and then thermally converted into polyimide films at 300 to 500 °C, usually 350 °C, in a nitrogen atmosphere. The polyimide films were then pulverized into molding powders which, in turn, were processed into neat resin discs at temperatures and pressures as high as 468 °C/34.5 MPa. Additional resin discs were processed with similar conditions from molding powders of some 3F monomer combinations that were prepared using other techniques as described in reference 3. These techniques included precipitation of the amic-acid molding powders from DMAc amic-acid 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 Tg's of these films and resin discs were then determined by thermomechanical analysis (TMA)

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and were the subject of a prior report (ref. 3) which identified two new polyimides of Tg ≥371 °C (3F dianhydride/paraphenylene diamine (PPDA), Tg ~370 °C, and pyromellitic dianhydride (PMDA)/3F diamine, Tg ~440 °C). The thermal and thermo-oxidative stability of these 3F polyimide films and the comparison 6F polyimide films were then determined by thermogravimetric analysis (TGA). The isothermal weight losses of the films and the resin discs at 316 °C, 371 °C, and also at 371 °C under 0.5 MPa (~5 atm) air pressure were then determined (using a weight loss/unit surface area basis). The results of these studies identified two new 3F containing polyimides (3F dianhydride/PPDA and 6F dianhydride/3F diamine) with low rates of weight loss/unit surface area compared to the known very oxidatively stable 6F dianhydride/PPDA and PMDA/6F diamine resins. The study also showed that the resin discs exhibited the same overall trends in weight loss/unit surface area as their respective films, however, the weight loss per unit surface area of the discs 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 discs compared to the films. These overall results indicate that polyimides containing the 3F linkage exhibit thermal and thermo-oxidative stability comparable to polyimides containing the 6F linkage. These thermo-oxidative stability results, combined with the prior Tg results (ref. 3), show that further development of the 3F connecting linkage in aryl dianhydride and aryl diamine monomers to produce high Tg, thermo-oxidatively stable polyimides suitable for 371 °C resin and composite applications continues to be warranted.

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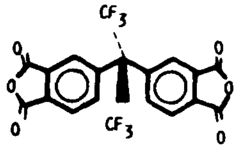
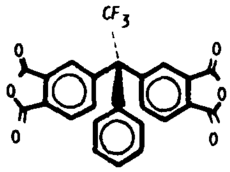


6F DIANHYDRIDE, 6FDA



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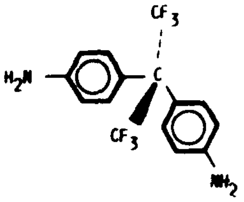
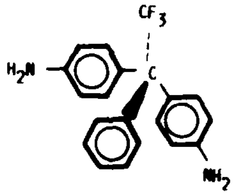


6F DIAMINE, 6FDAM



3F DIAMINE, 3FDAM

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16. Abstract

Nine new condensation polyimides containing the trifluorophenylethylidene linkage were synthesized by the amic-acid route. Several other polyimides, including some with the hexafluoroisopropylidene 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 °C, 371 °C, 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 discs. The discs were also characterized by T_gs and 316 and 371 °C isothermal weight losses. The film study identified two new polyimides with T_gs greater than 371 °C and two new polyimides with low rates of weight loss. The resin discs 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 voids or to mechanical degradation induced during preparation of the molding powders. The overall results indicate that polyimides containing the trifluorophenylethylidene linkage have T_gs and thermo-oxidative stability comparable to polyimides containing the hexafluoroisopropylidene group.

17. Key Words (Suggested by Author(s))

Polyimides; Condensation polymers; High temperature stability; Glass transition temperature (~~T_g~~); Thermally ~~and~~ thermo-oxidatively ~~stable~~

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