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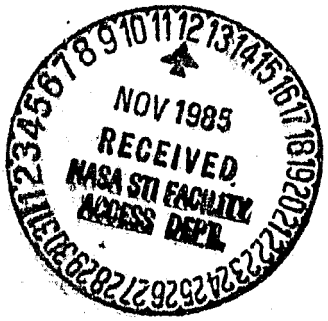

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STRUCTURE-TO-GLASS TRANSITION TEMPERATURE RELATIONSHIPS IN HIGH TEMPERATURE STABLE CONDENSATION POLYIMIDES

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SUMMARY

The presence of a hexafluoroisopropylidene (6F) connecting group in aryl dianhydrides used to prepare aromatic condensation polyimides provides high glass transition temperature (T_g) polyimides with excellent thermo-oxidative stability. The purpose of this study was to determine if a trifluorophenylethylidene (3F) connecting group would have a similar effect on the T_g of aromatic condensation polyimides. A new dianhydride containing the 3F connecting group was synthesized. This dianhydride and an 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 3F containing condensation polyimides. Known polyimides, including some with the 6F connecting linkage, were also prepared for comparison purposes. The new 3F containing polymers and the comparison polymers were prepared by condensation polymerization via the traditional amic-acid polymerization method in N,N-dimethylacetamide solvent. The solutions were characterized by determining their inherent viscosities and then were thermally converted into polyimide films under nitrogen atmosphere at 300 to 500 °C, usually 350 °C. The polyimide films were 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. The T_g's of the films and resin discs were then determined by thermomechanical analysis and were correlated as a function of the final processing temperatures of the films and resin discs. The results showed similarities existed in the T_g's depending on the nature of the connecting linkage in the monomers used to prepare the condensation polyimides. Specifically, the T_g results indicate the condensation polyimides containing the 3F connecting linkage have T_g's directly comparable to analogous condensation polyimides containing the 6F connecting linkage. The results also showed these T_g's were consistently higher than analogous polyimides containing smaller connecting linkages, such as oxygen, methylene, or carbonyl linkages. Thus, T_g's ~370 °C were obtained in polymers comprised of 3F dianhydride or 6F dianhydride/paraphenylene diamine and T_g's ~440 °C were obtained in polymers comprised of pyromellitic dianhydride/3F diamine or 6F diamine. These high T_g's indicate that a potential exists for 371 °C applications for polyimides containing 3F linkages.

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INTRODUCTION

Aromatic polyimides are well-known for their excellent thermo-oxidative stability, and "after almost two decades of sustained research and development, polyimides are virtually alone in their commercial viability as high temperature stable polymers" (ref. 1). The viability is primarily due to the availability and low cost of polyimide monomers, and the adaptability of the polymerization to provide polyimides in a variety of useful forms such as films, coatings, moldings, and binder solutions. Because of the absence of cross-linking during polymerization, the thermoplastic 6F containing condensation polyimides are tougher than thermosets and are melt fusible (ref. 2). The overall purpose in examining the 3F group was to determine if the 3F containing polyimides are potential alternate melt fusible resins that would meet or exceed the performance of analogous commercially available 6F containing polyimides. The immediate objective of this study was to prepare and characterize some new high temperature stable condensation polyimides containing the trifluorophenylethylidene (3F) linkage between aromatic rings of dianhydride and/or diamine monomers. The primary method of characterization in this study was determination of glass transition temperature (T_g) as a function of processing temperature. The 3F linkage being investigated is structurally similar to the hexafluoroisopropylidene (6F) linkage used in commercially available condensation polyimides. The 3F monomers have an advantage over 6F monomers in that the phenyl ring can be used as a site to introduce functional groups desirable for modification of polymer properties. Because 3F and 6F linkages tend to restrict rotation at the polymer connecting linkages, both should raise T_g compared to smaller linkages. Because of steric implication on T_g and the potential for thermo-oxidative stability similar to that obtained for 6F polymers, introduction of the 3F groups into the polyimide chain could lead to processable polymers with high T_g's and significant service life in films, resins, moldings, adhesives, and laminates. Use temperatures as high as 371 °C have been obtained for condensation polyimides containing 6F linkages (ref. 2). The overall goal of this study was to determine if the new 3F condensation polyimides possess sufficiently high T_g's to also be potentially useful in 371 °C environments.

RESULTS AND DISCUSSION

Polymerizations and Viscosities

The dianhydride and diamine monomers used in this study are shown in tables I and II, respectively. The combinations of dianhydrides and diamines polymerized and the inherent viscosities of the resulting polyamic-acid solutions are given in table III(a) to (c). With the exception of the three polymers containing 3FDA (table III(a) and (c)) and the four polymers containing m,m'- and/or p,p'-6FDAM (table III(b)), all of the monomer combinations produced high molecular weight polyamic-acids as shown by $\eta_{inh} > 0.45$ dL/gm. The low viscosities of the polyamic-acids containing 3FDA were likely due to the 3FDA being insufficiently pure (as described in experimental section) for the preparation of high molecular weight polymers. The low η_{inh} of the polyamic-acids containing m,m'- and/or p,p'-6FDAM were presumably due to the presence of the two strongly electron withdrawing trifluoromethyl groups in these 6F diamines. This would decrease the nucleophilicity of the diamine, and lower their polymerizability towards dianhydrides, resulting in lower molecular weight polymers. It is interesting to note in table III(b) that the inherent

viscosities of PMDA-containing polyamic-acid solutions progressively increase as the electron withdrawing effect of the fluorinated connecting linkages in the diamine decreases (electron withdrawal in p,p'-6FDAM > m,m'-6FDAM > 3FDAM). This indicates that the molecular weight attained in the polymerization reaction, as shown by η_{inh}, is related to the extent to which the electron withdrawing fluorinated connecting group decreases the nucleophilicity of the aromatic amino groups. Thus, p,p'-6FDAM with two trifluoromethyl groups attached as a para substituent is the weakest diamine and the least reactive for attaining high molecular weight polymers. The 6F group as a meta, rather than para, substituent in the diamine results in a slightly stronger diamine, and hence increased η_{inh}. The use of only one electron withdrawing trifluoromethyl group in 3FDAM results in a stronger diamine, and hence the highest η_{inh} in table III(b). The effect of amine strength on η_{inh} has been previously reported (ref. 3) for nonfluorinated electron withdrawn diamine monomers. It should be noted that these solution polymerizations were done for 1 hr at room temperature and those containing m,m'-6FDAM were done for 2 hr. The longer reaction times did not apparently lead to the formation of higher molecular weight polymers as η_{inh} still exhibited a trend related to the nucleophilicity of the fluorinated diamine monomer.

In the opposite case, use of four different dianhydrides with a constant diamine (3FDAM, table III(c)), did not show such a trend. This is because the reactivity of any dianhydride would be accelerated, rather than retarded, by the presence of strong electron withdrawing groups in the connecting linkage. Despite the low viscosities for the 3FDA, m,m'-6FDAM, and p,p'-6FDAM polyamic-acid solutions, the polymer molecular weights were sufficient to prepare polyimide films for determining the T_g's.

Glass Transition Temperatures

The T_g's of the polyimide films and discs in all the figures in this paper are shown as a function of the final processing temperature. The purpose in examining T_g as a function of processing temperature was to determine to what extent the T_g's could be increased solely by increases in processing temperature. This T_g/processing temperature information is desirable because of the need to identify high T_g aerospace resins that remain processable while introducing minimal thermal degradation during processing procedures. In this study, the films were processed under inert environment conditions, and the discs were processed with short-time exposure to higher temperatures. These processing techniques allow the resin to easily eliminate the volatile condensation products, to reach the ultimate T_g, and to provide a processed film or disc sample without prolonged exposure to high temperature, thus minimizing thermal degradation. This method of advancing T_g avoids the use of long oxidative postcure cycles which serves to introduce sites of degradative oxidative cross-linking, and ultimately shortens the useful lifetime of the resin in a high temperature environment.

This thermoplastic-like processing method applied to the new 3FDA containing polyimides resulted in T_g's that were quite similar to analogous 6FDA containing polyimides. Figure 1 shows that the combination of 6FDA with the nonlinear, nonplanar diamines, 3FDAM and ODA, results in both resins reaching a constant T_g (the ultimate T_g). The T_g of the analogous 3FDA polymers were as much as 20 °C below the T_g's of 6FDA/3FDAM or 6FDA/ODA, respectively, presumably due to the lower molecular weights of the 3FDA

polymers (as shown by the lower η_{inh} of 3FDA containing polyamic-acids in table III(a) and (c)). It can be assumed that the low 3FDA polymer T_g's would approach the analogous 6FDA polymer T_g's if the molecular weights had been higher. Similarly, a 20 °C lower T_g was observed in comparisons of 3FDA/PPDA and 6FDA/PPDA. However, in this case, the 3FDA/PPDA film was suitable for preparation of molding powder, and the discs processed at higher temperatures from this molding powder exhibited a T_g almost identical to that of 6FDA/PPDA. Both PPDA resins also exhibited a similar gradual increase in T_g with increasing processing temperature. For comparison purposes to this study, the literature (ref. 4) T_g's for the 6FDA/ODA and 6FDA/PPDA are 286 and 326 °C, respectively. The 286 °C T_g compares favorably to ~300 °C T_g of 6FDA/ODA in figure 1. The 326 °C T_g of 6FDA/PPDA is not in close agreement to the ~371 °C T_g of 6FDA/PPDA in figure 1, due to insufficient 300 °C initial processing temperature used in the literature (ref. 4). However, it may be concluded that 3FDA and 6FDA provide similar T_g's in analogous polymers when processed at identical temperatures.

The finding that similar T_g's are obtained for 3F and 6F containing polymers was even more apparent when the 3F and 6F connecting linkages were used in the diamine monomers, rather than the dianhydride monomers. As shown in figure 2, the variation of T_g with processing temperature for PMDA/3FDAM and PMDA/p,p'-6FDAM polymers provide almost identical T_g's in the 440 to 450 °C range. In addition, the other four lines in the 425 to 475 °C processing temperature region show similar high T_g's (all > 400 °C and as high as ~460 °C) are obtained by processing of resin discs from the following: (a) chemically imidized molding powder of polyamic-acid of PMDA/3FDAM, (b) low molecular weight monomers (molding powders of dimethyl ester of PMDA (PMDE) and 3FDAM), (c) thermally imidized molding powder of precipitated polyamic-acid of PMDA/3FDAM, and (d) precipitated polyamic-acid molding powders of PMDA/3FDAM. These results were not unexpected because only slight differences in T_g's should exist. As long as the polymer remained melt fusible, the same T_g should result no matter what polymerization reaction procedure is used. Although considerable differences may result in other properties, such as processability and stability, depending on the starting resin form, the T_g's were not dramatically affected (fig. 2).

The failure to obtain a T_g increase in 400 °C processing of PMDA/3FDAM molding powder, prepared from 350 °C film, points out the importance of retaining polymer melt fusibility. Without a sufficient increase in processing temperature, fusibility did not occur and the T_g remained at the 378 °C level of the precursor film processed at 350 °C. Instead, an increase to 427 °C disc processing conditions was required to advance the T_g to 407 °C. Reprocessing of 350 °C films rather than discs of PMDA/p,p'-6FDAM and 3FDAM at 400 °C and higher temperatures also provided increases in T_g (shown in fig. 2 as square symbols). It is also important to note that all the polymer T_g's tended to exhibit a linear relationship with the processing temperature (as shown in fig. 2) out to a 475 °C processing temperature, resulting in T_g's of ~440 to 450 °C. Attempts to achieve T_g > 440 to 450 °C by processing films and discs at 500 °C resulted in thermal decomposition as evidenced by severe darkening and a reduction in T_g. The T_g of PMDA/3FDAM films, PMDA/p,p'-6FDAM films and PMDA/3FDAM discs decreased from the 440 to 450 °C region to 401, 380, and 405 °C, respectively.

The reason for the high T_g's observed for the 3F and 6F containing polymers becomes more apparent by studying space filling molecular models of the 3F and 6F groups. Both connecting groups tend to restrict the rotational mobility compared to smaller connecting groups, such as methylene, oxygen, or carbonyl connecting groups. Consequently, it would be expected that the ultimate T_g of polymers containing 3F or 6F groups would be higher than the T_g of polymers which do not contain the bulky, rotation restricting 3F or 6F linkages. Figure 3 shows such a trend where the ultimate T_g is higher for polyimides with increasing amounts of 3F or 6F linkage (T_g 6FDA/3FDAM > T_g 6FDA/ODA > T_g BTDA/ODA). As shown in figure 4, polymers with MDA instead of ODA also produce a similar increase in ultimate T_g with increasing amounts of 3F or 6F linkages (T_g 6FDA/3FDAM > T_g 6FDA/MDA > T_g BTDA/MDA). By comparing figures 3 and 4, it can be seen that all the polymers appear to reach their ultimate T_g with the exception of the MDA containing polymers. The continued increase in T_g of the MDA polymers is due to thermally induced cross-linking of the methylene connecting linkage (ref. 5). The literature T_g's for the BTDA/ODA and MDA (ref. 3) polymers are 279 and 290 °C, respectively, and the 6FDA/ODA and MDA (ref. 4) polymers are 285 and 291 °C, respectively. All are in close agreement to the ultimate T_g's of these polymers shown in figures 3 and 4.

The effect of introducing one bulky 3F or 6F monomer into a polymer on raising the T_g is dramatic, even when changing from a carbonyl connecting linkage such as in BTDA/MDA or ODA to a 6F linkage in 6FDA/MDA or ODA (see figs. 3 and 4). However, the increase in T_g by the use of a 3F or 6F group in both monomers such as when changing from a BTDA/3FDAM to 6FDAM/3FDAM was considerably less, as shown by the lower two lines in figure 5. The ultimate T_g of 6FDA/3FDAM is only slightly higher than the T_g of BTDA/3FDAM. This is presumably because of the following: (a) the carbonyl tends to create some partial stiffness in the polymer chain due to its conjugation with at least one BTDA aromatic ring at a time, and (b) both polymers already contain one bulky 3F or 6F group so the T_g is already increased dramatically before adding a second 3F or 6F group (as in 6FDA/3FDAM). Thus it may be concluded that the use of the bulky nonlinear, nonplanar 3F or 6F group with any nonlinear, nonplanar monomer results in a higher T_g than for the use of smaller linkages, such as methylene, oxygen, or carbonyl.

However, the T_g of the doubly sterically hindered 6FDA/3FDAM can be significantly increased by replacement of one of the bulky nonlinear, nonplanar 3F or 6F monomers with a linear-planar monomer. Replacement of the nonlinear, nonplanar 3FDAM in 6FDA/3FDAM by linear-planar PPDA raises the T_g to the 370 °C region (see fig. 1) while replacement of the nonlinear, nonplanar 6FDA in 6FDA/3FDAM by linear-planar PMDA further raises T_g to the 440-450 °C region (see fig. 2). As shown in comparisons of the upper four lines of figure 5, these T_g's (> 400 °C) are significantly higher than the ultimate T_g's of analogous PMDA polymers containing the smaller connecting linkages present in ODA and MDA (T_g PMDA/3FDAM or p,p'-6FDAM > T_g PMDA/ODA > T_g PMDA/MDA). This trend is similar to the trend observed in BTDA and 6FDA based polymers (see figs. 3 and 4). For comparison purposes to this study, the literature (ref. 3) T_g's for the PMDA/MDA and PMDA/ODA are 357 and 361 °C, respectively. The 357 °C T_g compares very favorably to the ~360 °C T_g of PMDA/MDA in figure 5. The 361 °C T_g is not in close agreement to the ~400 °C T_g of PMDA/ODA in figure 5, due to the insufficient 300 °C processing temperature used in the literature (ref. 3). Thus, it may be concluded that the use of the bulky nonlinear, nonplanar 3F or 6F group with a

linear-planar dianhydride results in a higher T_g than for the use of smaller linkages, such as methylene, oxygen, or carbonyls.

It should be noted that all of the PMDA T_g's are greater than or equal to the T_g of the only other polymers containing a linear-planar unit, PPDA in 3FDA/PPDA and 6FDA/PPDA. The greater T_g's of PMDA containing polymers may be speculated to result from the larger planar ring size of the linear tricyclic PMDA unit in PMDA/3FDAM (or ODA, MDA) versus the smaller planar ring size of the linear monocyclic PPDA unit in 3FDA/PPDA or 6FDA/PPDA. However, no clear-cut evidence exists to identify what may be the cause of the very high PMDA/3FDAM or p,p'-6FDAM T_g's. One could also speculate that the PMDA T_g's are higher due to the increasing processing temperatures causing any on the following: (a) the last traces of imide formation into a linear-planar tricyclic ring, (b) high temperature cross-linking reactions, or (c) a higher degree of order in the polymers. However no evidence exists to support any of these additional speculations. The literature (ref. 6) even suggests the increased T_g of PMDA containing polymers may be due to an increased amount of charge-transfer complexes in the bulk state, rather than primarily resulting from increases in processing temperature as this study seems to indicate.

To achieve T_g's > 400 °C with the PMDA/3FDAM or p,p'-6FDAM system, processing temperatures of 425 to 475 °C are needed. Processing at these temperatures can be considered to be detrimental to stability as well as difficult to conduct from an engineering standpoint. Consequently, two approaches were investigated to allow lower temperature processing. The first approach is to lower the PMDA content by using some 6FDA or BTDA, and the second approach is to lower the p,p'-6FDAM content by using some m,m'-6FDAM. The latter approach has been reported for nonfluorinated diamine containing BTDA polymers (ref. 3). Thus the effect of employing these approaches on T_g was predictable and resulted in a lowering of the T_g of PMDA/3FDAM. The results of employing the first approach are illustrated in figure 6. It can be seen that the use of mixed dianhydrides clearly result in T_g's intermediate between the fully PMDA polymer and the non-PMDA polymer. The gradual increase in T_g as a function of increasing processing temperature for the mixed BTDA/PMDA polymer suggests that the BTDA may be undergoing thermal cross-linking. However, there is no direct evidence to support this speculation. In fact, only a constant ~320 °C T_g versus processing temperature was observed for BTDA/3FDAM (without PMDA as in figs. 5 and 6). The results of employing the second approach are illustrated in figure 7. It can be seen that the use of mixed m,m'-6FDAM with 3FDAM or p,p'-6FDAM clearly results in T_g's intermediate between the fully PMDA/3FDAM or p,p'-6FDAM polymer and the PMDA/m,m'-6FDAM polymer. The use of lesser amounts of nonlinear, nonplanar dianhydride or m,m'-diamines may be necessary to achieve increased processability/fusibility for fabrication of larger resin or composite samples than the resin discs or films in this study. The use of isomeric diamines was used for commercial 6FDA/PPDA composites (ref. 2) in which 5 percent of the PPDA was replaced by meta-phenylenediamine.

A comparison of the extent of the reductions in T_g's in figures 6 and 7 shows that introduction of the m,m'-6FDAM into PMDA/3FDAM polymers provides a greater reduction in T_g than for introduction of BTDA or 6FDA into PMDA/-3FDAM polymers. The complete change from the p,p'-6FDAM or 3FDAM to m,m'-6FDAM resulted in a very significant lowering of 150 to 160 °C in T_g (from 440-450 to 290 °C) as seen in figure 7. The complete change from PMDA to BTDA or 6FDA resulted in a slightly less but still significant lowering of 120 to 130 °C

in T_g (from 440-450 to ~320 °C) as seen in figure 6. The larger reduction in PMDA polymer T_g's resulting from the use of m,m'-diamines, compared to the use of dianhydrides containing a connecting linkage, is in agreement with the literature (ref. 6). In this study it is likely that the chain packing of PMDA/3FDAM or p,p'-6FDAM is disrupted more by introducing the nonlinear, nonplanar meta,meta' linked 6FDAM than for introducing the nonlinear, nonplanar 6FDA or BTDA (with essentially a net meta,para' linkage effect). In other words, the more dominant factor causing T_g reduction in this case is believed to be the introduction of a nonlinear, nonplanar, m,m'-structure for a nonlinear, nonplanar p,p'-structure (as with the diamines). This resulted in a greater effect than for the introduction of a structure halfway between m,m'- and p,p'- (a net meta,para' effect) for a linear, planar structure (as with the dianhydrides). However, both molecular changes are disruptive to the molecular ordering of the PMDA linear-planar units affecting the chain packing of the solid polymer, hence resulting in a lowering of T_g's. Similar observations about PMDA containing polymers in the literature (ref. 6) attempt to explain the T_g effect on the basis of charge-transfer interactions.

An important point to notice is the inherent stability of all of the T_g's of the polymers shown in figures 1 to 7. The polymers either maintain their ultimate T_g or show increases in their T_g with increases in processing temperature. Only two exceptions were noted to this behavior. First, preparation of a PMDA/3FDAM or p,p'-6FDAM films after 1 hr at 500 °C under nitrogen no longer continued to show an increase in the T_g's. Instead the T_g's fell to 401 and 380 °C, respectively, while the films underwent severe darkening and embrittlement. The shorter time exposure to 500 °C in disc processing apparently did not cause as much degradation as with the films as the T_g only fell to 415 °C. However, it did show that the ultimate T_g of PMDA/3FDAM disc was in the 440 to 450 °C region because a further increase in T_g did not result with the increased processing temperature. These thermal degradations with longer exposure to high temperatures were not unexpected.

The second exception to obtaining a constant or increasing T_g with increases in processing temperature was observed with the use of BDAF. Figure 8 shows that discs processed at successively higher temperatures from molding powder prepared from 350 °C processed PMDA/BDAF films resulted in a successively lower T_g for each disc in spite of the short-time high temperature processing cycle used. The T_g of the ground-up film used to prepare the discs was 345 °C by DSC determination, which is in good agreement with the T_g of 360 °C by TMA determination before grinding. Thus grinding was not the cause of the even lower T_g's of the processed discs. However, formation of PMDA/BDAF films, rather than discs, at similar higher processing temperatures, but longer processing times, resulted in significantly higher T_g's (shown as circle symbols in fig. 8). These T_g's finally reached an ultimate T_g of ~460 °C. A further increase in processing temperature to 500 °C resulted in a decrease of the PMDA/BDAF T_g to the 380-390 °C region due to the thermal degradation during the 3 hr heatup-hold-cool down processing cycle used for the film preparation. Attempts to advance the T_g's by reprocessing 350 °C film showed that the T_g remained constant until a 500 °C reprocessing temperature was used, after which the T_g increased to the 400-420 °C region. In order to explain these discrepancies, the resin discs fabricated at 400, 427, and 454 °C were subjected to the same 3 hr thermal cycle used for films processed at these temperatures. This resulted in increasing the lower T_g's of the discs towards the higher T_g's of the films (shown by triangle

symbols in fig. 8). This unusual time-temperature activity in the T_g behavior of the discs and films indicates that the BDAF monomer is thermally unstable and the high T_g's that result are caused by extensive thermal cross-linking during processing. Thus the cross-linking can be accomplished by long-time thermal formation of films, thermal reprocessing of films, and long-time thermal processing of resin discs. Currently T_g's over 400 °C are also obtained for PMDA/BDAF by extensive postcure cycles at 371 °C in air (ref. 7) rather than thermal cycles as described in this study.

CONCLUSIONS

From the results of this study the following may be concluded:

1. The presence of the 3F connecting linkage in condensation polyimides in either the dianhydride or diamine monomer leads to high T_g's that are virtually identical to similar polymers containing the 6F connecting group.

2. Condensation polyimides containing the 3F or 6F connecting linkages provide T_g's that increase with increasing 3F or 6F content compared to similar polymers that contain smaller connecting linkages, such as methylene, oxygen, and carbonyl connecting linkages.

3. The high T_g's (> 440 °C) of the PMDA/3FDAM polymers may be attained by several polymerization methods such as using 3FDAM with either PMDA or the dimethyl ester of PMDA. Similar high T_g's (> 400 °C) can also be attained by processing starting from different forms, such as processing PMDA/3FDAM polyamic-acid molding powder or processing chemically or thermally imidized PMDA/3FDAM molding powder.

4. As a processing aid, the high T_g's of PMDA/3FDAM or p,p'-6FDAM may be varied to intermediate T_g's in a controllable manner by partially replacing PMDA with nonlinear, nonplanar dianhydrides or by partially replacing 3FDAM or p,p'-6FDAM with meta,meta'-isomeric 6F diamines.

5. The use of the BDAF monomer appears to act as a site for thermal decomposition during film and disc processing conditions. This degradation initially lowers T_g but subsequently causes large increases in T_g, presumably by thermally initiated cross-linking.

Experimental

Monomers. - The dianhydride of 1,1-bis[4-(1,2-dicarboxyphenyl)]-1-phenyl-2,2,2-trifluoroethane (3FDA) was prepared by a three-step synthesis. Using a procedure analogous to one patented by Kray and Rosser (ref. 8), α,α,α-trifluoroacetophenone was stirred with an excess of o-xylene and an equimolar amount of trifluoromethanesulfonic acid (based on trifluoroacetophenone) for several days at room temperature, during which time the product precipitated. After isolation by suction filtration and recrystallization from 50/50 heptane/-benzene, a 75 to 80 percent yield of 1,1-bis[4-(1,2-dimethylphenyl)]-1-phenyl-2,2,2-trifluoroethane (3FTM) was obtained, mp 177 to 178 °C. The ^1H and ^{13}C NMR and IR spectra were consistent with the assigned structure. The 3FTM was oxidized with potassium permanganate to the tetraacid by the general procedure of Marvel and Rassweiler (ref. 9). Because the tetraacid, recovered in low

yield (~25 percent), was very hygroscopic and difficult to purify, it was converted directly to 3FDA by treatment with hot acetic anhydride. The yields of this reaction were also low (~25 percent). The best sample of 3FDA was crystallized from cooled acetic anhydride and vacuum dried at 60 °C to obtain mp 204-206 °C. The tetraacid and 3FDA were not fully characterized although HPLC of the tetraacid indicated the oxidation was complete and ^{13}C NMR on a tetraacid sample, and IR spectra of both compounds were consistent with the assigned structures.

1,1,-Bis(4-aminophenyl)-1-phenyl-2,2,2-trifluoroethane (3FDAM) was synthesized by the procedure of Kray and Rosser (ref. 10) as modified by Alston (ref. 11). For this polymer study, the 3FDAM was initially recrystallized from chloroform using charcoal to remove the purple color. Then it was recrystallized twice from absolute ethanol and vacuum dried at 50 °C to obtain mp 216-217.5 °C (lit. mp 217-217.5 °C) (ref. 11).

The dianhydrides, PMDA, and BTDA, were obtained from commercial sources, and the 6FDA was prepared as per the literature procedure (ref. 12). The three dianhydrides were then sublimed at approximately 200 °C and 0.5 torr before use.

The diamines, PPDA, ODA, MDA, and BDAF were obtained from commercial sources, and all except BDAF were recrystallized twice from absolute ethanol and vacuum dried at 50 °C before use. The m,m'-6FDAM was supplied from an experimental source and recrystallized once from heptane to mp 76-77 °C lit. (ref. 13) mps 108-111 °C and 84.5-85.5 °C. HPLC before and after the recrystallization from heptane showed that the trace of m,p'-6FDAM was removed. The p,p'-6FDAM was synthesized under contract (ref. 14) and used as obtained, mp 195-196 °C, lit. mp 197 °C (ref. 15).

Polymers. - The N,N-dimethylacetamide (DMAc) which was used as the polymerization solvent was freshly distilled from calcium hydride at 85 °C and 75 torr. The synthesis of each polyimide film was accomplished in two steps via the polyamic-acid according to the general procedure of Sroog, et al. (ref. 16). The solid dianhydride was added rapidly to an equimolar amount of the diamine dissolved in enough DMAc to make 33.3 gm of a solution containing 15 percent w/w solids. After stirring for 1 hr at room temperature (2 hr for those containing m,m'-6FDAM), the resulting polyamic-acid solution was stored at -10 °C under nitrogen until it was converted into a polyimide film. Inherent viscosities (η_{inh} in dL/g) at 25 °C were calculated for the polyamic-acid solutions, diluted to 0.5 percent w/v solids, using the equation $\eta_{inh} = (1/C)\ln(t/t_o)$. Each polyimide film was prepared by placing 4.0 gm of the polyamic-acid solution in a 60 mm diameter petri dish; evaporating the solution at 80 °C under flowing nitrogen; and imidizing the resulting polyamic-acid film at a maximum temperature of 300 to 500 °C, usually 350 °C, also under flowing nitrogen. In the final step, a 3 hr cycle of 1 hr heatup, 1 hr at temperature, and 1 hr cool down was used. The polyimide films were pulverized with a Wig-L-Bug to obtain molding powders for conversion into neat resin discs.

In the case of PMDA/3FDAM polymer, molding powders were also prepared by several other techniques for comparison purposes. The polyamic-acid molding powder was prepared by addition of the DMAc polyamic-acid solution into ice-cold water. The resulting solids were collected, washed with water and dried at 50 °C. Some of the polyamic-acid PMDA/3FDAM molding powder was thermally

converted to PMDA/3FDAM polyimide molding powder by subjecting it to 3 hr heat-hold-cool cycle described for film preparation (to a maximum temperature of 400 °C). PMDA/3FDAM polyimide molding powder was also prepared by a chemical, rather than thermal, imidization procedure by which the DMAc polyamic-acid solution was added to 1:1 (v/v) acetic anhydride:pyridine and stirred at room temperature for 2 hr. The solution was then added dropwise into ice-cold water, the precipitate was collected by filtration, washed with water and dried at 50 °C. Another PMDA/3FDAM molding powder was also prepared by dissolving in methanol equimolar amounts of dimethyl ester of PMDA (PMDE) and 3FDAM, followed by evaporation with gentle heating of the methanol until a syrup remained, followed by treatment at 260 °C for 1 hr in an air circulating oven.

All of the molding powders (monomer mixtures, polyamic-acid, chemically imidized, thermally imidized and ground up polyimide films) were converted into neat resin discs by high temperature compression molding. In a typical procedure for pressing resin discs, 600 to 1000 mg, usually about 800 mg of molding powder was loaded into a 21 mm diameter matched metal die. The cold die was placed in a press that had been preheated to a temperature about 25 °C above the desired final processing temperature. When the temperature of the die reached 300-350 °C (~4 min), a pressure of 3.45 MPa was applied, and the pressure was doubled each minute while the heat-up continued until a final pressure of 27.6 or 34.5 MPa was attained. After another 3 to 4 min, the desired final processing temperature of 399 to 468 °C was reached and the heat was shut off. The pressure was maintained for at least 30 min until the temperature of the die was below 150 °C, after which the pressure was released and the die was disassembled.

Techniques. - Glass transition temperatures (T_g) of the films and resin discs were obtained by thermomechanical analysis (TMA) at a heating rate of 20 °C/min. T_g's were also obtained for some films by differential scanning calorimetry (DSC) at a heating rate of 20 °C/min. The T_g and processing temperatures were reproducible to less than $\pm$2 °C for an individual sample. Greater variations in T_g between samples were considered to represent real differences.

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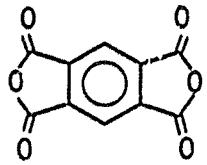
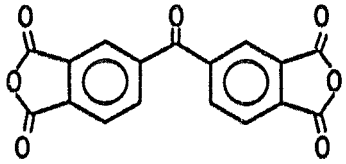
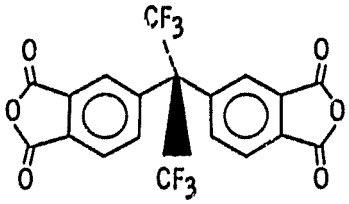
TABLE I. - DIANHYDRIDE MONOMERS IN CONDENSATION POLYIMIDES



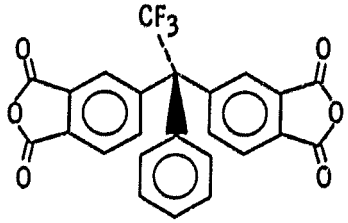
PMDA
Pyromellitic Dianhydride



BTDA
3, 3', 4, 4'-Benzophenone Tetracarboxylic Dianhydride

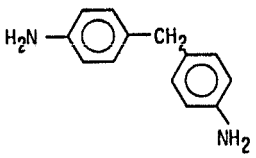


6FDA
4, 4'-(Hexafluoroisopropylidene) Bis(Phthalic Anhydride)

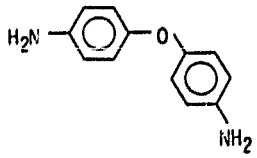


3FDA
4, 4'-(1-Phenyl-2, 2, 2-Trifluoro-ethylidene) Bis(Phthalic Anhydride)

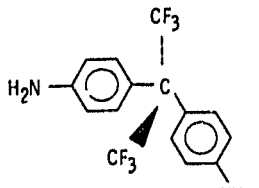
TABLE II. - DIAMINE MONOMERS IN CONDENSATION POLYIMIDES



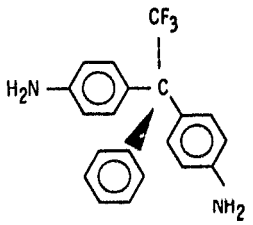
MDA
4, 4'-Methylene dianiline



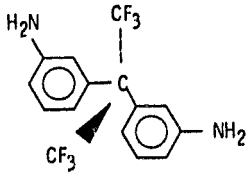
ODA
4, 4'-Oxydianiline



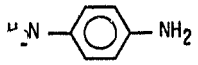
p, p'-6FDAM
2, 2-bis(4-Aminophenyl)Hexafluoropropane



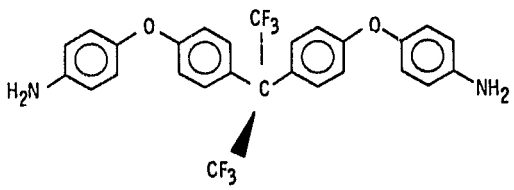
3FDAM
1, 1-Bis(4-Aminophenyl)-1-Phenyl -2, 2, 2-Trifluoroethane



m, m'-6FDAM
2, 2-Bis(3-Aminophenyl)Hexafluoropropane



PPDA
Paraphenylenediamine



BDAF
2, 2-Bis[4-(4'-Aminophenoxy)phenyl]Hexafluoropropane

TABLE III.

(a) Inherent viscosities[a] of polyamic-acid solutions.

	ODA	MDA	PPDA	BDAF
PMDA	0.89	Gel	---[b]	0.88
BTDA	0.91	0.80	---[b]	---[b]
6FDA	0.98	1.52	0.99	---[b]
3FDA[c]	0.21	---[b]	0.30	---[b]

(b) Inherent viscosities[a] of a PMDA/3FDAM and 6DAM polyamic acid solutions.

	p,p'-6FDAM	50/50 p,p'-6FDAM/ m,m'-6FDAM	m,m'-6FDAM	50/50 m,m'-6FDAM/ 3FDAM	3FDAM
PMDA	0.29	0.35	0.38	0.42	[d]0.53 0.72

Decreasing Electron Withdrawl ⟶

(c) Inherent viscosities[a] of polyamic-acid solutions resulting from polymerizations of 3FDAM with various dianhydrides

	3FDA[c]	PMDA	BTDA	6FDA	50/50 PMDA/BTDA	50/50 PMDA/6FDA
3FDAM	0.14	[d]0.53 0.72	0.87	0.73	0.45	0.79

[a] η_{inh} in dL/g determined at 0.5 percent w/v in DMAc at 25 °C.
[b] Not polymerized.
[c] Low η_{inh} due to marginal purity of 3FDA.
[d] Minimum of three fold larger scale polymerization than any other.

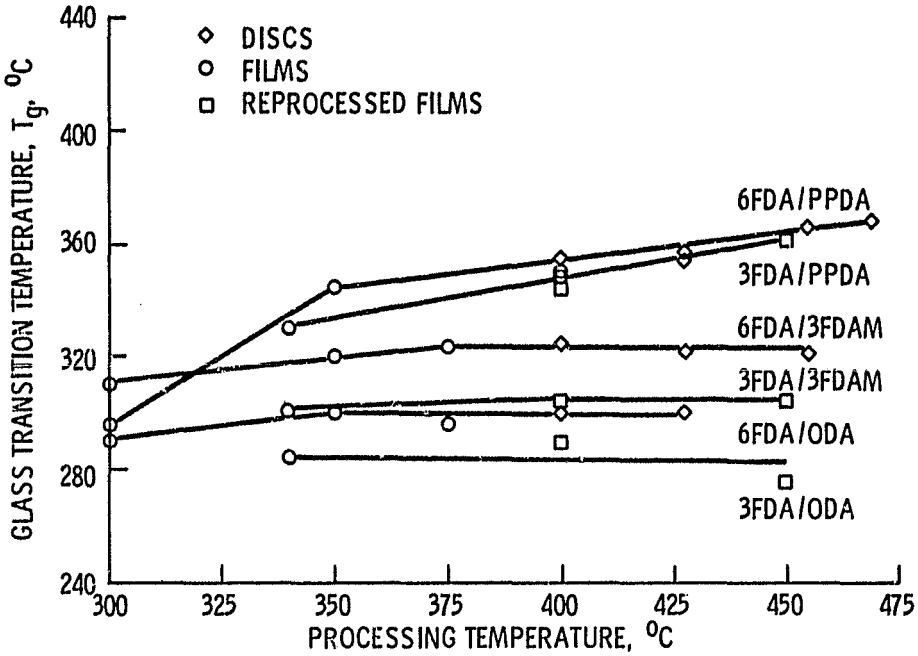


Figure 1. - Effect of 3FDA and 6FDA on polyimide T_g's.

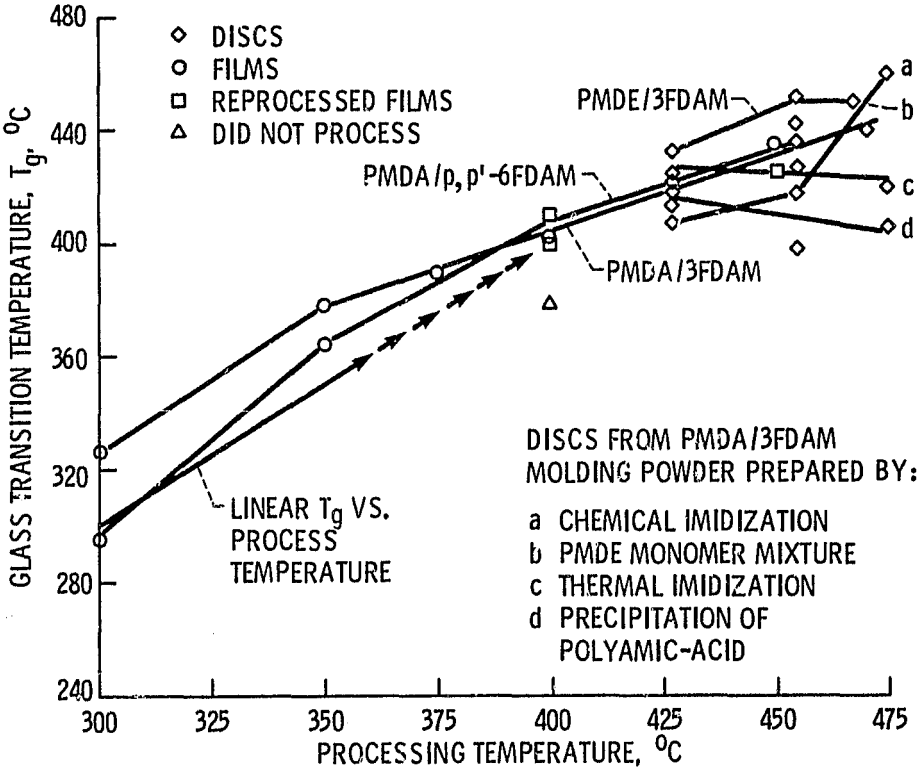


Figure 2. - Effect of 3FDAM and p,p'-6FDAM on polyimide T_g's.

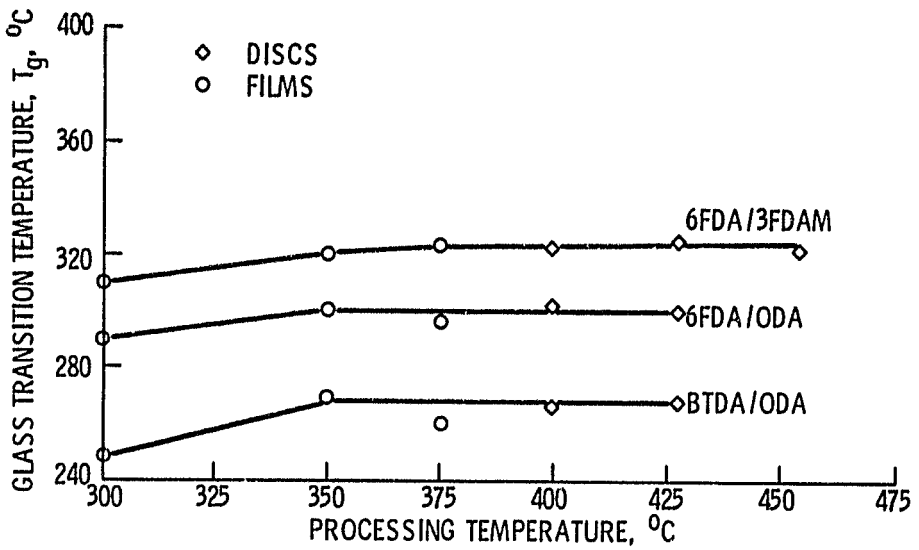


Figure 3. - Effect of connecting group size on polyimide T_g's.

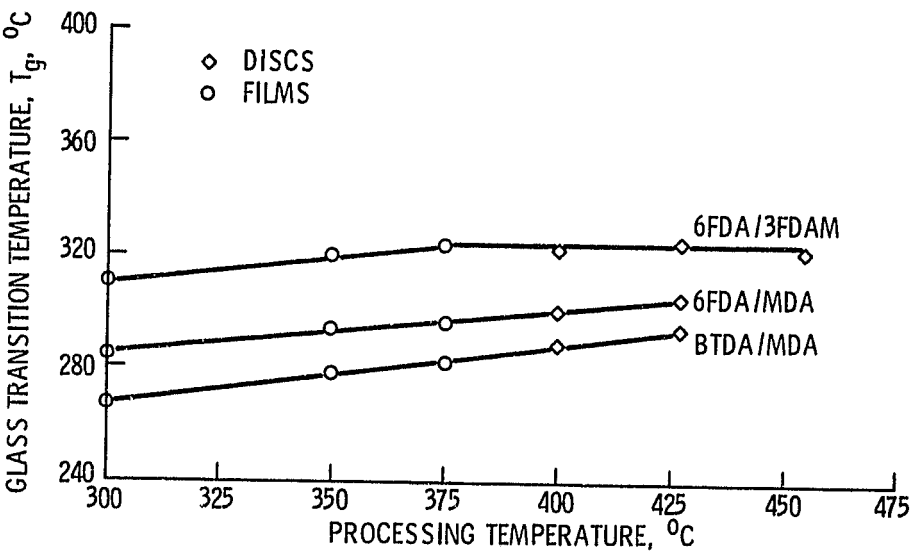


Figure 4. - Effect of connecting group size on polyimide T_g's.

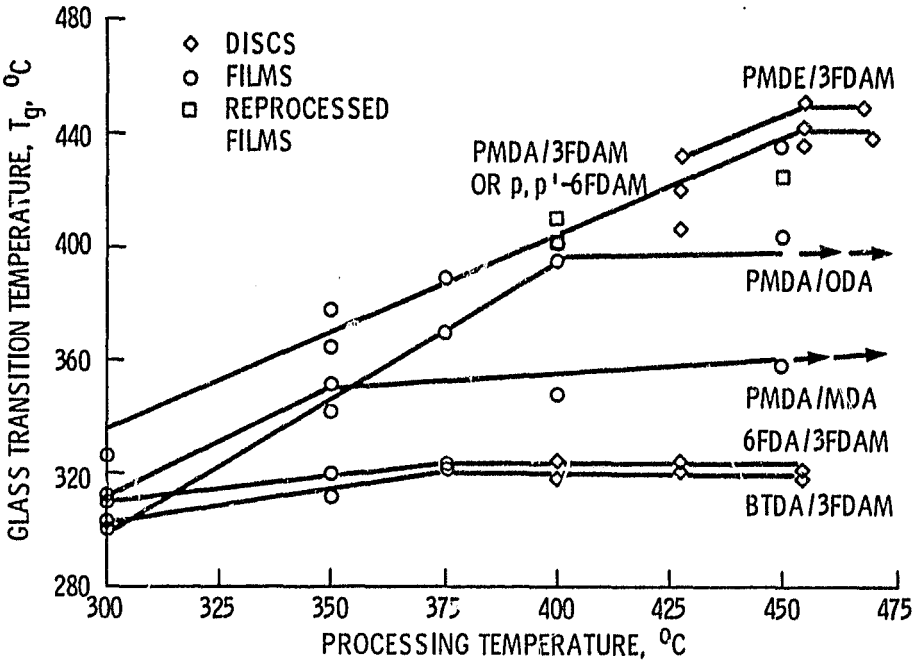


Figure 5. - Effect of diamine connecting group size and dianhydride planarity-linearity on polyimide T_g's.

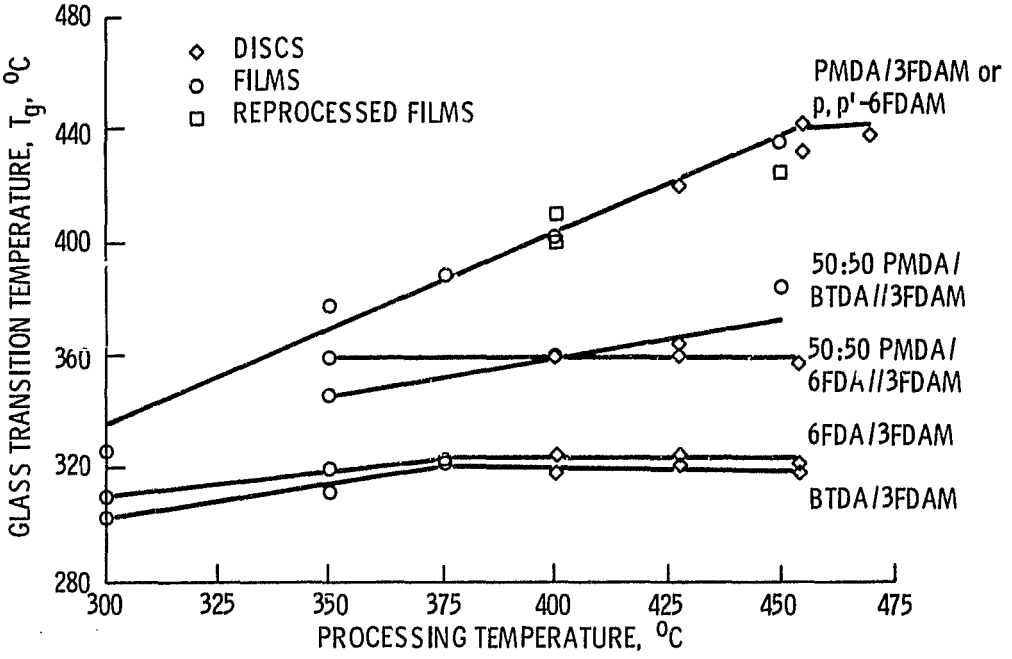


Figure 6. - Effect of various dianhydrides on 3FDAM polyimide T_g's.

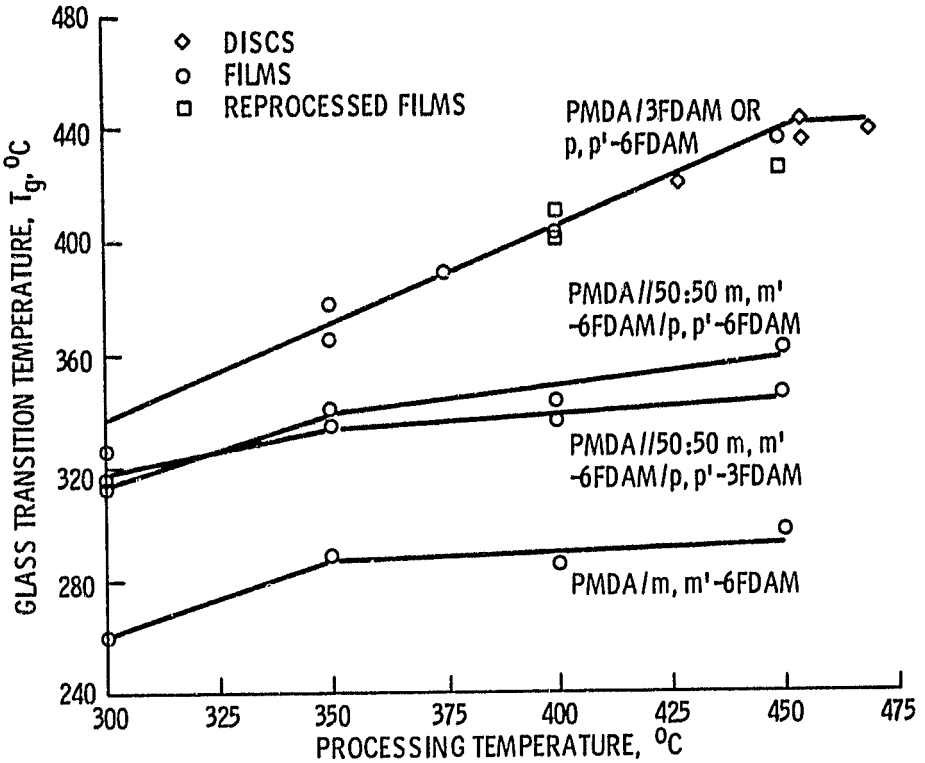


Figure 7. - Effect of various 3F and 6F diamines on PMDA polyimide T_g's.

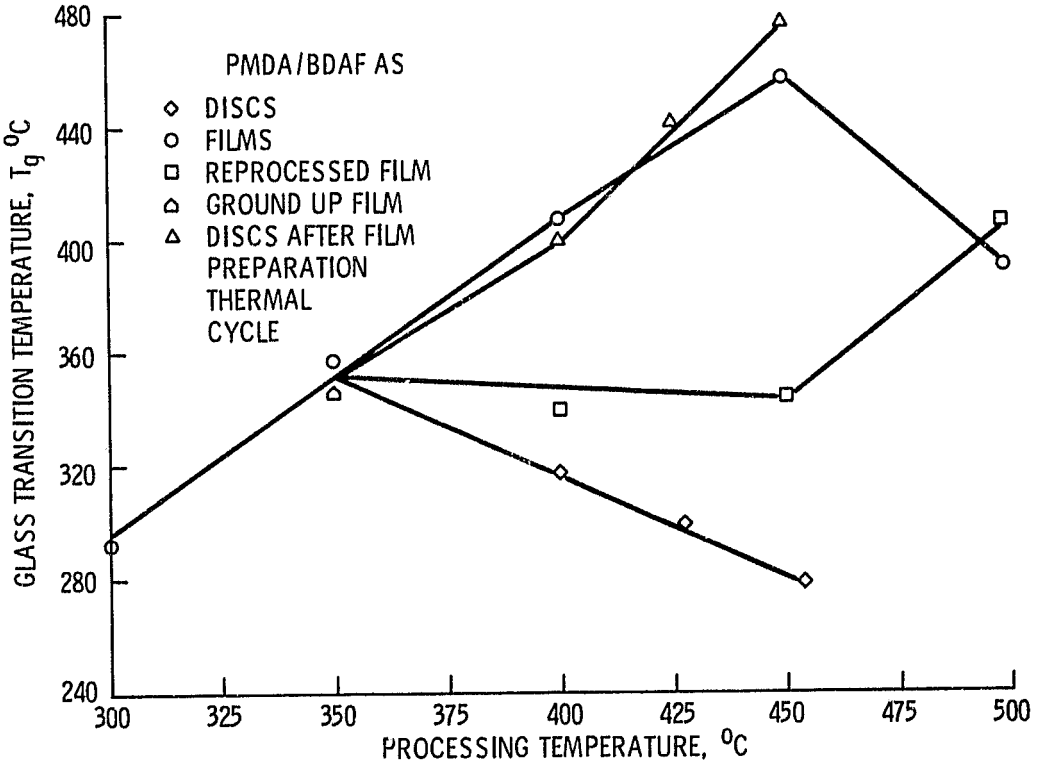


Figure 8. - Effect of processing conditions on PMDA/BDAF polyimide T_g's.

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15. Supplementary Notes

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16. Abstract

The presence of a hexafluoroisopropylidene (6F) connecting group in aryl dianhydrides used to prepare aromatic condensation polyimides provides high glass transition temperature (T_g) polyimides with excellent thermo-oxidative stability. The purpose of this study was to determine if a trifluorophenylethylidene (3F) connecting group would have a similar effect on the T_g of aromatic condensation polyimides. A new dianhydride containing the 3F connecting group was synthesized. This dianhydride and an 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 3F containing condensation polyimides. Known polyimides, including some with the 6F connecting linkage, were also prepared for comparison purposes. The new 3F containing polymers and the comparison polymers were prepared by condensation polymerization via the traditional amic-acid polymerization method in N,N-dimethylacetamide solvent. The solutions were characterized by determining their inherent viscosities and then were thermally converted into polyimide films under nitrogen atmosphere at 300 to 500 °C, usually 350 °C. The polyimide films were 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. The T_g's of the films and resin discs were then determined by thermomechanical analysis and were correlated as a function of the final processing temperatures of the films and resin discs. The results showed similarities existed in the T_g's depending on the nature of the connecting linkage in the monomers used to prepare the condensation polyimides. Specifically, the T_g results indicate the condensation polyimides containing the 3F connecting linkage have T_g's directly comparable to analogous condensation polyimides containing the 6F connecting linkage. The results also showed these T_g's were consistently higher then analogous polyimides containing smaller connecting linkages, such as oxygen, methylene, or carbonyl linkages. Thus, T_g's ~370 °C were obtained in polymers comprised of 3F dianhydride or 6F dianhydride/paraphenylene diamine and T_g's ~440 °C were obtained in polymers comprised of pyromelletic dianhydride/3F diamine or 6F diamine. These high T_g's indicate that a potential exists for 371 °C applications for polyimides containing 3F linkage.

17. Key Words (Suggested by Author(s))	18. Distribution Statement
Polyimides; Glass transition temperature (T_g); Condensation polymers; High temperature stable; Thermally stable	Unclassified - unlimited STAR Category 27

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