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Advanced Polymers Containing the Phenyltrifluoroethylidene Connecting Group

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Abstract

A new, lower cost fluorinated dianhydride based on the phenyltrifluoroethylidene (3F) connecting linkage was invented by the principal author in the early 1980's. New 3F condensation and addition cured polyimides were synthesized with the newly discovered 3F dianhydride and the previously known 3F diamine. As controls, polyimides based on the somewhat analogous higher cost hexafluoroisopropylidene (6F) linkage were also prepared. The short term thermal oxidative stability (TOS), determined by thermal gravimetric analysis (TGA), and the glass transition temperatures (Tg) of 3F dianhydride polyimides were found to be similar to 6F dianhydride polyimides, but the Tg was slightly higher for 3F diamine polyimides than 6F diamine polyimides. Unfortunately, in real time testing, long term TOS of 3F polymers was clearly inferior to 6F polymers. This was due to a 3 to 5 fold greater rate of loss of trifluoromethyl group from 3F versus 6F linkages. However, at shorter times or lower temperatures, 3F TOS was almost comparable to 6F TOS. The wide scope of the 3F technology was also demonstrated to have distinct unique advantages over 6F technology through the use of the 3F pendant phenyl ring as a synthetic site to introduce other functional groups. These groups have been used for the control or modification of polymer properties; an advantage lacking within 6F technology. The synthetic ease by which 3F can be introduced into various types of monomers has lead to the explosion of advanced 3F polyimides and other high performance advanced 3F polymers in the prior decade of 3F polymer literature as cited herein; covering polyimides, substituted polyimides, at least ten types of nonpolyimide 3F polymer modifications, and also the government's nine 3F U.S. patents and corporations' nine 3F U.S. patents.

1. Introduction

The commercially available condensation polyimide (known as AVIMID N®) containing the hexafluoroiso-propylidene (6F) connecting linkage is considered to be state-of-the-art in ultimate thermo-oxidative stability (TOS) for organic polymer matrix resins. Improvement in the 6F based polyimide useful lifetime at temperatures up to 371 °C (700 °F) is desirable for increased polyimide composite usage in jet engine applications. All types of advanced lightweight materials, including high temperature polyimide composites, are needed because their use in structural and engine applications will result in significant weight and fuel savings. The main objective of this study was to examine the somewhat analogous phenyltrifluoroethylidene (3F) connecting linkage in polyimides to determine if the 3F linkage provides improved glass transition temperature (Tg), TOS and composite mechanical properties compared to 6F; making 3F a potential replacement candidate for 6F technology in long term, high temperature environments, such as in jet engines. Another objective of this paper is to demonstrate the scope of 3F monomer/polymer synthesis capability in order to educate additional researchers about 3F technology for use in potential projects and other applications. The third objective of this paper is to bring together in

one article a 3F review/summary using the latest and/or most complete 3F publications as lead references. This review portion of the paper will highlight current state-of-the-art 3F technology, recent progress in 3F research, current 3F applications, such as microelectronics and gas separator membranes, and will describe our 3F work aimed ultimately toward composites in jet engine applications.

2. Experimental

2.1 3F Dianhydride and Diamine Monomers

The 3F and 6F dianhydride and diamine monomers used in this study are shown in figure 1. Also used were dianhydrides containing carbonyl linkages (3,3',4,4'-benzophenone tetracarboxylic dianhydride, (BTDA)) and ether linkages (3,3',4,4'-oxydiphthalic dianhydride, (ODPA)), along with diamines containing ether linkages (4,4'-oxydianiline, (ODA)), and without linkages (para-phenylenediamine, (PPDA)). In order to study the 3F linkage, this principal investigator invented the synthetic route to the new 3F dianhydride (3FDA)[1–5] (fig. 2) and synthesized[1] and patented[6] many new 3F polyimides. The 3FDA monomer synthesis route closely follows the synthesis route of the commercially available 6F dianhydride (6FDA), using an air oxidation process identical to the commercial synthesis of 6FDA, to provide an 85% yield of 3FDA. The only change in the 3FDA synthesis route is the use of lower cost, less toxic starting material, α,α,α-trifluoroacetophenone (TFA), rather than 1,1,1,3,3,3-hexafluoroacetone (HFA) or hexafluoropropylene oxide (HFPO), for preparing the 3F tetramethyl precursor in 90% yield before oxidation to the 3FDA. Alternatively to air oxidation, the oxidation to 6FDA may use nitric acid. This is not desirable for the 3F oxidation step, as nitration of the pendant 3F phenyl ring also occurs;[7] (6F does not nitrate as it does not contain a pendant phenyl ring). Others have used and patented[8] the nitric acid oxidation route to 3FDA but only after additional oxidation product cleanup is performed to acquire unnitrated 3FDA. For other polymer uses (described later in sections 3.3.3 to 3.3.5), however this high reactivity of the 3F pendant phenyl can be desirable, even to the point of deliberately nitrating the pendant 3F phenyl ring as in reference 7. This phenyl can be a useful site to introduce other functional groups (besides nitro) to prepare substituted 3F monomers[7, 9–10] and substituted 3F polymers[9] to alter or control the subsequent 3F polymer properties.

The first laboratory synthetic route to the existing 3F diamine[11] (3FDAM) used a one step synthesis by reacting aniline with TFA using aniline hydrochloride catalyst (fig. 3). Initially, this investigator scaled up that procedure to a half pound size and improved the purification and yield to 80%.[1–5, 7] Others, in academia, have further improved the synthesis, purification, and yield of 3FDAM.[12] At the same time, the Defense Advanced Research Projects Agency (DARPA) supported additional 3FDAM synthesis and polymerizations under Army Research Office (ARO) monitorship.[13] This interest arose because of both the lower cost, one step, higher yield 3FDAM synthesis route, and the increased 3FDAM reactivity compared to the expensive, multi-step, low yield synthesis of 6F Diamine (6FDAM), and the very low 6FDAM reactivity. The low reactivity of 6FDAM is due to the strong electron withdrawing nature of the 6F group.[1, 14–15]
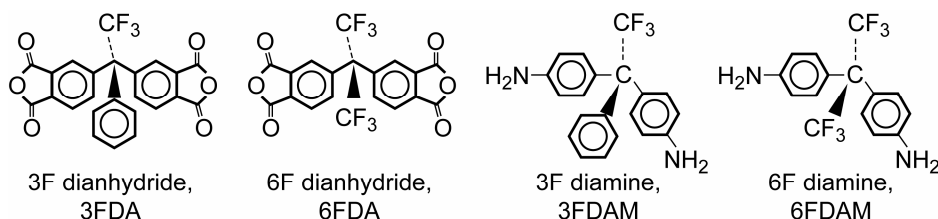

Figure 1.—3F and 6F dianhydride and diamine monomers used in this investigation.
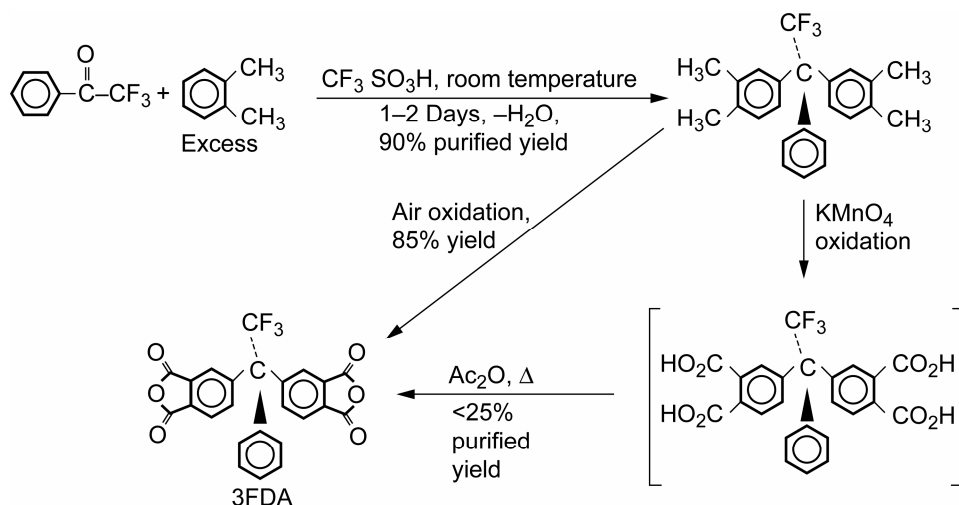
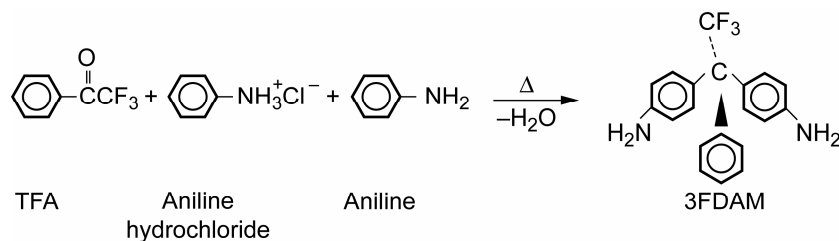Figure 2.—Synthesis route to the new 3F dianhydride monomer.

Figure 3.—Synthesis route to known 3F diamine monomer.

2.2 3F Polyimide Polymers and Composites

Various new condensation and addition cured polyimide resins containing PPDA and 3FDA, as well as the corresponding 6FDA (as controls), were synthesized[16] for weight loss investigations at 260, 316, and 371 °C (500, 600, and 700 °F). Specifically for this study, two different lots of 3FDA and 6FDA as diacid dimethylesters (3FDE and 6FDE)/PPDA/phthalic anhydride (PA) molding powders formed at n/n+1/2 stoichiometry (n = 113.34 for 3F and n = 115.21 for 6F), were processed as 10.16 by 10.16 cm neat resin plaques. The 3F and 6F polymerization of monomeric reactants (PMR) molding powders had been endcapped with PA to limit the maximum calculated formulated molecular weight (FMW) to 60,000. The process conditions were twenty minutes at 415 °C (779 °F) under 3.45 MPa pressure (500 psi). The two lots of each resin plaque making four different plaques were each cut into forty nine 1.29 by 1.29 cm squares and used to greatly exceed the minimum requirements for a statistically designed postcure study to determine the optimum temperature (from 371 to 468 in 14 °C intervals) and environment (air versus argon) required to obtain the best postcure. The results showed the best postcure (lowest weight loss) was at the lowest temperature in an inert environment. After postcure both lots of the 3F and 6F resin squares were used for aging in air for 400 hr at 371 °C.

Neat resins of 3FDAM and 6FDAM, besides 3FDA and 6FDA, were also used for this study. Specifically, PMR monomer solutions of 3FDAM, 6FDAM, and ODA with ODPA, BTDA, 3FDA, and 6FDA as diacid dimethylesters were prepared using PA as the endcap to limit the maximum calculated FMW to 60,000. A portion of each of the calculated 60,000 FMW PMR solutions was evaporated to dryness, making the PMR molding powders. Resin disks (2.54 cm diameter) of each powder were processed by inserting the cold powder filled die into a 427 °C press and applying 27.6 MPa (4000 psi) in evenly spaced 3.45 MPa increments so that final pressure was reached by 371 °C, after which heating was stopped, the insulation removed, and a final mold temperature of 382 to 418 °C (well above all the Tgs)

was momentarily reached before the mold started to rapidly cool back to room temperature. Later the discs were cut into four 0.64 by 0.64 cm squares to use as long term aging samples (after postcuring the squares in air for 20 hr at 316 °C) and the edge pieces used for short term thermal analysis (Tg and thermal gravimetric analysis, (TGA)). Many of these resins were also processed at these temperatures as discs between two rheometric plates using only enough pressure to fuse the melted molding powder to the rheometric plate, to be later used to determine the remelt processability viscosity as described later in section 3.1.4.

Composites and neat resin plaques were also prepared at a calculated 20,000, 40,000, and 60,000 FMW using PA endcaps to limit the maximum FMW to these values. The resins selected, using the results of the above neat resin study and remelt viscosity study, were a low cost selection of ODPA/ODA, a medium cost selection of ODPA/3FDAM and a high cost selection of 6FDA/3FDAM. The neat resins were processed as 10.16 by 10.16 cm moldings from molding powders as a preliminary measure of the temperature/pressure needed to consolidate the powders, from which uniform processing conditions (below) were decided on. For the composites study, all the PMR monomer solutions were prepregged at forty resin weight percent on drum wound unsized G30–500 carbon fiber. Twelve ply 7.62 by 20.32 cm unidirectional composites were prepared using both a compression molding cycle and two slightly different simulated autoclave molding cycles, all reaching 343 °C momentarily at a final pressure of 1.38 MPa (200 psi) for simulated autoclave moldings or 3.45 MPa for compression moldings and then allowed to cool to room temperature under those pressures. The laminates were ultrasonically C-scanned for quality analysis and cut into nominally 2.54 by 6.75 cm pieces for mechanical testing and aging studies. All the pieces were postcured in a circulating air oven for 20 hr at 316 °C.

2.3 Thermal and Mechanical Characterization

The 3F and 6F resins and composites were characterized for maximum potential, long-term use temperature by isothermal aging (ITA), TGA, and Tg determinations. Fourier transform infrared spectroscopy (FTIR) was coupled to a TGA (TGA-FTIR) to identify the high temperature degradation products and elucidate the degradation pathways of 3F and 6F polyimides. Interlaminar shear strength (ILSS), flexural strength (FS), and flexural modulus (FM) testing of unidirectional graphite fiber composites were performed using American Society for Testing and Materials (ASTM) procedures prescribed in D2344–76 and D790–71.

3. Results and Discussion

3.1 Thermoplastic 3F Condensation Polyimides

In our very early 3F studies, emphasis was on identifying high Tg and high TOS thermoplastic[1,16] and thermoset 3F polyimides[17–19] using traditional solution condensation polymerizations and also the PMR approach to fabricate 3F and 6F films,[1] resin disks[16–17] and graphite fiber composites[18–20] that were either unendcapped[1] high molecular weight formulations or PA endcapped thermoplastics (this paper) or nadic ester (NE) endcapped BTDA/3FDAM[17–20] thermosets. Others then joined the 3F bandwagon by preparing 3F thermosets of NE endcapped 3FDA/4,4'-methylenedianiline[21] (MDA), NE endcapped 3FDA/PPDA,[22] and unsubstituted and phenyl substituted ethynyl endcapped 3,3',4,4'-biphenyl dianhydride (BPDA)/3FDAM[13] as resins and composites while others prepared PA endcapped 3F thermoplastics of 3FDA/PPDA[23] and pyromellitic dianhydride (PMDA)/3FDAM[24] resins. However the major initial interest was in PMDA/3FDAM thermoplastics[24] because of the very high Tg (> 430 °C) for PMDA/3FDAM thermoplastic polyimide and similar high Tgs for PMDA/3FDAM-meta or para 6FDAM copolyimides, all first reported by this principal author.[1] These were so desirable that the very high Tg of PA endcapped PMDA/3FDAM was later reconfirmed by others.[24] The Tg's of BTDA,[1] 3FDA,[1] 6FDA,[1, 25] and BPDA[25]/3FDAM polyimides were lower, so our further interest in these was minimal. Others[25–26] also

used mixed dianhydrides of PMDA/6FDA with 3FDAM[25] and mixed diamines of 3FDAM/PPDA with PMDA or BPDA[25] and mixed diamines of 2,2-bis[4-(4-aminophenoxy)phenyl]-1,1,1,3,3,3-hexafluoropropane (BDAF)/3FDAM with PMDA[26] to produce high Tg PA endcapped copolyimides.[25–26] These resins are similar or identical to earlier PMDA/BDAF and mixed dianhydrides of PMDA/6FDA and PMDA/BTDA with 3FDAM and mixed diamines of 3FDAM/6FDAM with PMDA which produced the high Tg unendcapped polyimides and copolyimides reported in our initial study.[1] Our initial[1] and later 3F publications[27–28] and technology transfer publications[29] and subsequent work of others[24–26] eventually lead to heightened interest in 3F, which then lead to sponsorship by DARPA, under ARO monitorship.[13] This project had an eventual goal of high temperature jet engine 3FDAM bushings comparable to the state-of-the-art 6FDA/PPDA commercial bushings. Later, this DARPA study[13] culminated in combining BPDA/3FDAM/meta-phenylethynylaniline (PEA) endcapped thermosets and PA endcapped thermoplastics to prepare 3F semi-interpenetrating networks (SIPN) for study as composites. At this point most studies claimed high TOS and high Tg, but these studies had been spread in so many different directions by additional investigators that proper comparisons of definitive data were becoming elusive. Thus, this paper will attempt to bring together all 3F polymer data in some form of a comparative fashion and conclusion.

3.1.1 Glass transition temperatures (Tg's)

For 3F to be a potential replacement for 6F, it is necessary for the 3F Tg to at least equal, or better yet, exceed the 6F Tg in order for 3F polyimides to possess equally useful high temperature mechanical properties before polymer chain segmental rotation occurs at the Tg. Using the Tg's from our seminal publication,[1] table 1 shows that 3F Tg equals or exceeds 6F Tg by two different methods for determining Tg, differential scanning calorimetry (DSC) under 1.38 MPa nitrogen pressure and thermal mechanical analysis (TMA), (both at 10 °C/min heatup rate). The Tg's of 3FDA versus 6FDA polyimides are virtually identical, while the Tg's of 3FDAM versus 6FDAM polyimides are consistently higher by around 15 to 30 °C, depending on which method was used. Thus, 3FDAM polyimides exhibited a higher potential polymer use temperature than 6FDAM polyimides, while also clearly placing the 3FDAM Tg much higher than the Tg of ODA polyimides (with small ether linkages) and slightly higher than the Tg of PPDA (without any diamine linkage) in commercially available unpostcured AVIMID N®. These observations suggest that the larger 3F linkage caused greater restricted polymer chain segmental rotation, resulting in the higher 3F Tg's. A portion of the 3FDAM Tg increase could also be due to 6FDAM not achieving very high molecular weight polymers, but in either case, the 15 to 30 °C higher 3FDAM Tg's were one strong factor in DARPA's initial 3FDAM interest.[13]

TABLE 1.—COMPARISON OF 3F AND 6F Tg's WITH EACH OTHER AND WITH ODA AND PPDA								
DIAMINE	3FDAM		6FDAM		ODA		PPDA	
	TMA	DSC	TMA	DSC	TMA	DSC	TMA	DSC
DIANHYDRIDE	°C	°C	°C	°C	°C	°C	°C	°C
3FDA	308	293	279	275	288	283	292	—
6FDA	309	287	287	271	264	266	300	—

3.1.2 Thermal Gravimetric Analysis (TGA)

For 3F to be a potential replacement for 6F, it is necessary also for the 3F TOS to be at least equal, or better yet, exceed the 6F TOS in order for 3F polyimides to possess equally useful high temperature lifetimes as 6F polyimides. Using TGA at 10 °C/min heatup in air as a preliminary TOS measurement, table 2 shows 3F TOS equals or exceeds 6F TOS. The onset of weight loss via TGA for the 3FDA versus 6FDA polyimides is virtually identical, while the onset of weight loss for 3FDAM versus 6FDAM polyimides is around 5 °C higher. Thus, 3FDAM polyimides could be slightly more thermally oxidatively stable than 6FDAM polyimides. In addition, 3FDAM TOS is much higher than ODA TOS (because of

ODA's less stable ether linkages) and comparable to the TOS of PPDA based commercially available AVIMID N®. These observations suggest the 3F linkage provides excellent short term TOS via TGA. A portion of the small 5 °C 3FDAM increase could also be due to 6FDAM not achieving very high molecular weight polymers, but in either case, the higher 3FDAM TOS was also a factor in DARPA's strong 3FDAM interest.[13]

TABLE 2.—COMPARISON OF 3F AND 6F ONSET OF WEIGHT LOSSES
IN AIR WITH EACH OTHER AND WITH ODA AND PPDA

DIAMINE	3FDAM	6FDAM	ODA	PPDA
DIANHYDRIDE	°C	°C	°C	°C
3FDA	524	516	496	521
6FDA	521	517	519	522

Later, a subsequent more exhaustive TGA study[23] of the stability of 3FDA versus 6FDA/PPDA/PA polyimides was done using four kinetic analysis methods to determine the activation energy (Ea) of decomposition, instead of just using onset of weight loss as in table 2. Unfortunately, this clearly provided a different stability result; that 3F is inferior to 6F polymers. The Ea in kJ/mol of these polymers showed 3F was inferior by all four analytical methods in reference 23 (109 versus 140 by Coats and Redfern, 84 versus 162 by Ingrahm and Marier, 123 versus 162 by Horwitz and Metzger, and 142 versus 171 by ITA). Figure 4 shows representative TGA's done in nitrogen from this later study. These clearly demonstrate the higher char yield but slightly lower decomposition temperature (T_d) of 3F compared to 6F/PPDA/PA polyimide, which resulted in the lower Ea for 3F. The TGA is also in agreement with the postcuring data done in inert and air environments as shown in figures 5 and 6. If one views the postcure weight losses as a series of high resolution TGAs (each stopping at a set temperature until the weight loss is completed), then the T_d and Ea data is consistent with the dynamic TGA data (fig. 4) and the inert postcure weight loss data (fig. 6 with only one resin lot shown and fig. 5 with two resin lots plotted in which the lot 2 closed triangles are superimposed on top of the lot 1 open triangles). The T_d and Ea agree because they are determined in similar temperature ranges from the data in figures 4 to 6. It is only at much higher temperatures that the final char yield of 3F exceeds 6F, well beyond the temperature range in which the T_d and Ea are determined, thus accounting for the better 6F TOS T_d and Ea. The 3F postcure weight loss in both air and inert environments was higher until 441 °C (825 °F),
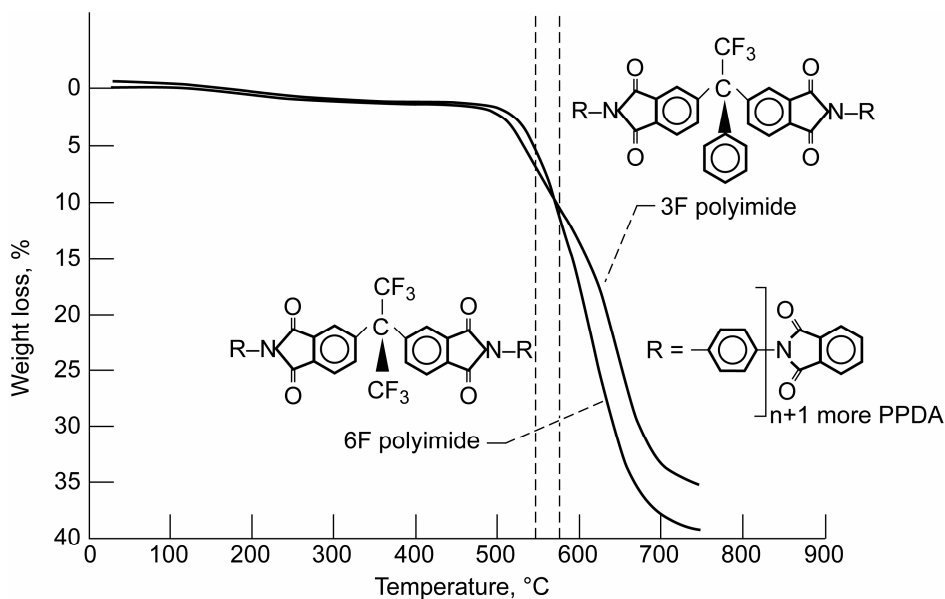

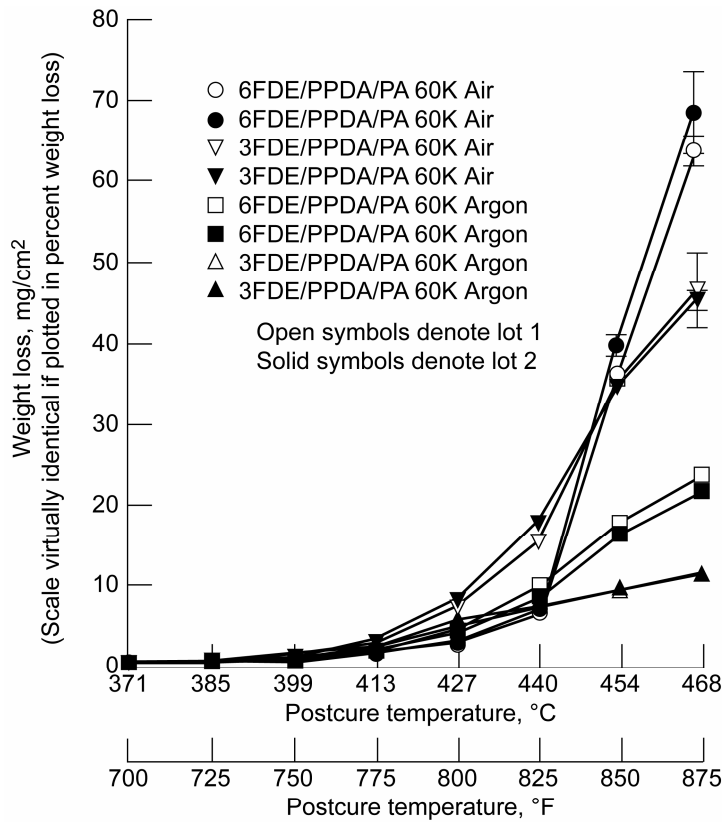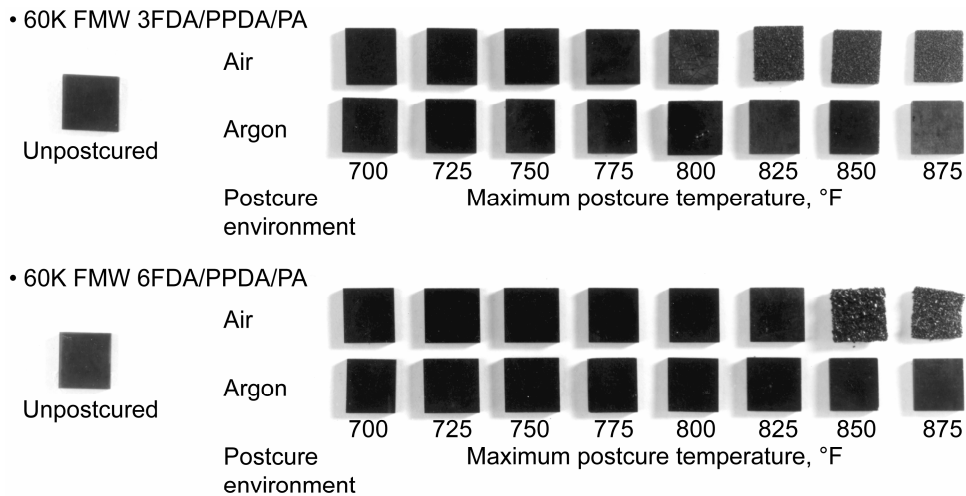Figure 4.—TGA's in nitrogen of 3FDA versus 6FDA/PPDA polyimides.

Figure 5.—Statistically designed postcure study of 3FDE and 6FDE/PPDA/PA resins in air and argon atmospheres.

- 60K FMW 3FDA/PPDA/PA

Unpostcured

- 60K FMW 6FDA/PPDA/PA

Unpostcured

- All samples were approximately one-half inch squares cut from four inch square neat resin plaques that had been processed twenty minutes at 415 °C (780 °F) under 3.45 MPa (500 psi). After processing, all samples were postcured by ten hour linear heatup from room temperature to maximum postcure temperature, then eight hours hold at maximum postcure temperature and slow cooling back to room temperature. Each sample postcured in air or argon atmospheres.

Figure 6.—Postcuring of 3FDA and 6FDA/PPDA/PA resins at 371 to 482 °C (700 to 875 °F) in 14 °C (25 °F) increments in air or argon.

resulting in lower 3F T_d. Above 441 °C 6F postcure weight loss exceeded 3F, thus leaving 3F with a greater char yield at the final TGA temperature in figure 4 and also at the higher postcure temperatures as shown in figure 5. Visually, the 3F and 6F resins postcured in inert environment, shown in figure 6, look similar at all postcure temperatures. However, visually the air postcured 3F samples, also shown in figure 6, show more cracks at lower postcure temperature to increase the surface area. This alone could account for the greater 3F weight loss seen early on (thus providing lower 3F T_d in air). However, 3F did eventually provide a lower overall postcure weight loss than 6F. As the 6F surface cracking increased (fig. 6), the resulting 6F postcure weight loss (fig. 5) was greater than that of 3F at the higher postcure temperatures.

The higher char yield of 3F versus 6F in both the inert TGA environment and in the air and inert postcure environments led us to examine these samples in a microcalorimetry experiment[30] utilized for screening the flammability of plastics. The experiment was done under nitrogen at a very rapid heatup rate (4.3 °C/s), with a 30 second hold at the final 930 °C temperature. Again, 3F had a higher char yield versus 6F as shown in table 3. Thus, the microcalorimetry data is consistent with the TGA (fig. 4) and postcure weight loss data (fig. 5) discussed above in section 3.1.2. Unfortunately a higher (poorer) heat capacity and greater total heat release was also found for 3F (table 3). This is considered to be the real measure of comparative flammability. The higher 3F total heat release indicates that 3F was clearly not as good in preliminary flammability tests as 6F. Not surprisingly, nonfluorinated polyimides were even poorer, as also shown in table 3. Thus 6F is again superior to 3F.

TABLE 3.—MICROCALORIMETRY DATA FOR 3FDA, 6FDA,
AND NONFLUORINATED CONDENSATION POLYIMIDES

Polyimide	Heat Capacity, J/g-k	Total Heat Release, $K^{J/g}$	Char Yield, %
6F/PPDA/PA	17±3	2.0±0.3	59.3
3F/PPDA/PA	20±2	3.8±0.3	66.3
Typical Nonfluorinated Polyimide	25±3	6.6±0.3	51.9

Data is average of three determinations for one milligram samples heated at 4.3 °C/sec to reach 930 °C, then held at 930 °C for 30 sec.
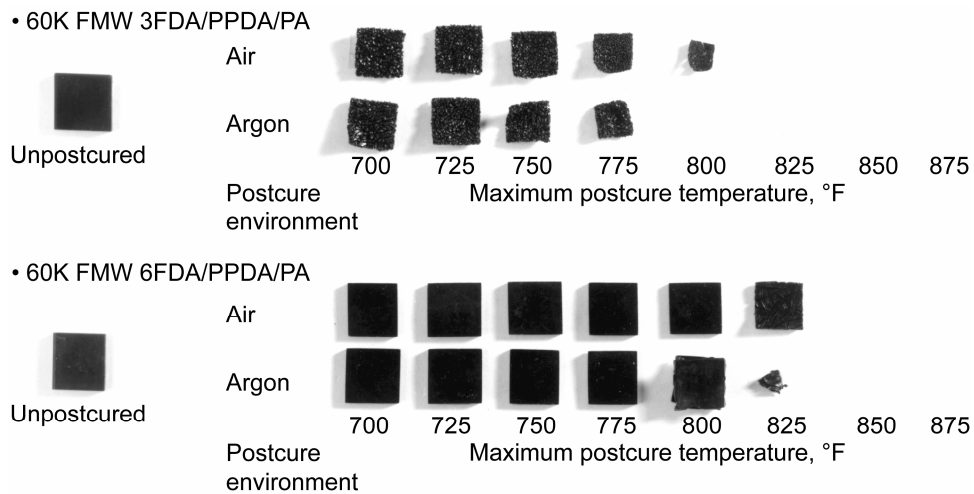
3.1.3 Isothermal Aging (ITA)

After postcuring, the Tg of both 3FDA and 6FDA/PPDA/PA can be raised to be satisfactory for 371 °C applications. However, the promising preliminary TGA TOS result, when studied in real time ITA showed 3FDA was clearly inferior to 6FDA. In our initial study of 400 hr aging at 371 °C in two different ovens, the weight losses of two resin lots (table 4) for commercial AVIMID N® was 7.5 to 8.1% versus 14.2 to 16.0% for PMR laboratory prepared 6FDA/PPDA/PA while a shocking 93.5 to 99.9% for laboratory prepared 3FDA analog. This somewhat unexpected result clearly differs from earlier literature[31–34] in which others claim 3F is as stable or superior to 6F. Because of this discrepancy with our study, new 3FDA and 6FDA/PPDA/PA samples were prepared as described in the experimental section. The new samples were postcured as shown earlier in figures 5 and 6 and then aged. The visual effect of 200 and 400 hr aging at 371 °C (700 °F) is seen in figures 7 and 8. After even the mildest postcure conditions (371 °C in argon), the visual effect is apparent as a discoloration and severe dimensional shrinkage. The weight loss data through 300 hr aging is shown in figure 9. Interestingly, only the 6FDA weight loss after either air or argon 371 °C postcure remains linear if plotted to 400 hr while all the others continue to accelerate, with many of the samples having totally disappeared before 400 hr of aging (see fig. 8), after which all aging was discontinued. All three aging figures 7 to 9 clearly show increasing the postcure severity (seen in figs. 5 and 6) only further increases sample deterioration during subsequent aging with 3F degradation far exceeding 6F degradation. This agrees with our conclusions that 3F is not as stable as 6F.[23] To explain the different stability result of references 31 to 34 versus ours in reference 23, an extensive comparison in reference 23 of their sample compositions as to endcap type and
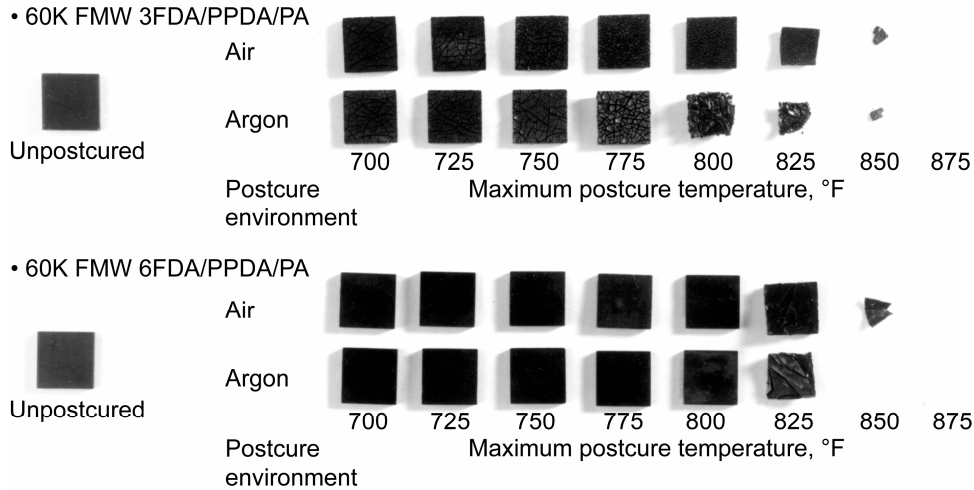
Figure 7.—Aging of 3FDA and 6FDA/PPDA/PA resins after 200 hours at 371 °C (700 ºF).

Figure 8.—Aging of 3FDA and 6FDA/PPDA/PA resins after 400 hours at 371 °C (700 ºF).

meta-phenylenediamine (MPDA) content, along with doing weight loss comparisons only at the same limited aging time at which they terminated their studies shows our weight loss results in reference 23 are quite similar at that aging time (100 hr at 371 °C), again supporting our sample validity and conclusion of 3F is less stable than 6F. When aged to times beyond those in references 31 to 34, the conclusion is more apparent. In fact, their own data[31–34] even supports this. They show that the stability of 3F/6F copolyimides increases as the amount of 3FDA used decreases. Thus, by all data, the thermal stability of 3F at 371 °C is clearly inferior to that of 6F.
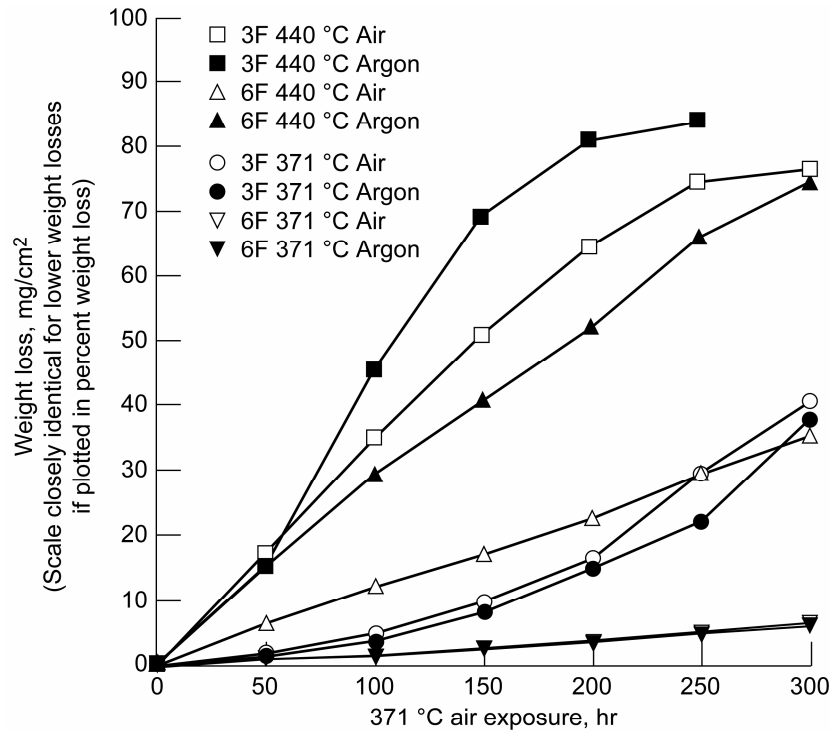
Figure 9.—Effect of postcure temperature and postcure environment on subsequent 371 °C (700 °F) aging weight losses of 3FDA and 6FDA/ PPDA/PA resins

TABLE 4.—371 °C WEIGHT LOSSES OF 3F VERSUS 6F RESINS

Resin	Percent resin weight loss after 384 hr at 371 °C (700 °F)	
	Oven No. 1	Oven No. 2
6FDA/PPDA[a] (Commercial AVIMID N®)	7.45±0.54	8.06±1.24
6FDE/PPDA/PA[b]	16.04±0.49	14.17±0.79
3FDE/PPDA/PA[b]	99.92±0.99	93.47±2.04

[a]High molecular weight condensation polyimide processed and provided by DuPont.
[b]Formulated for 60 000 M.W. using PMR approach, actual M.W. assumed to be significantly lower.

Even at a lower 316 °C (600 °F) aging temperature, figure 10 demonstrates the same trend of poorer 3FDA TOS. Also, AVIMID N® is now identical to laboratory prepared 6FDA/PPDA/PA (shown as solid circles). Regretfully, figure 10 also shows the same trend continues at an even lower 260 °C (500 °F) aging temperature, after extended aging of 10,000 hr. Invariably, the 3FDA/PPDA/PA resin and composites exhibited inferior high temperature stability (higher weight loss) in the 260 to 371 °C region desired for use in jet engines compared to the 6FDA/PPDA/PA resin and composites. A TGA-FTIR study[23] also clearly showed that the lower TOS of the 3F thermoplastic polyimide is due to the evolution of a 3 to 5 fold greater amount of trifluoromethane than the corresponding 6F polyimide or the two 6F based thermoset polyimides. This is easily seen in the TGA-FTIR at the 350 to 600 °C temperature range (fig. 11). Thus, 3F linkages clearly thermally decompose at a faster rate compared to 6F. This clearly compromises the potential of 3F polymers for high temperature jet engine composite applications.
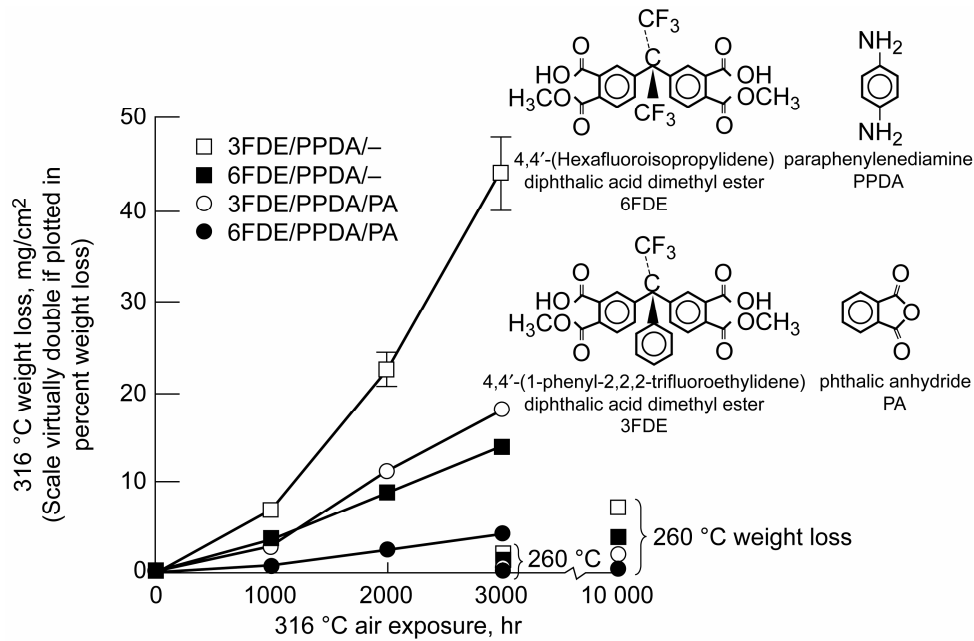
Figure 10.—Isothermal weight losses at 260 °C and 316 °C (500 and 600 °F) of 3FDE and 6FDE/PPDA/PA polyimides.
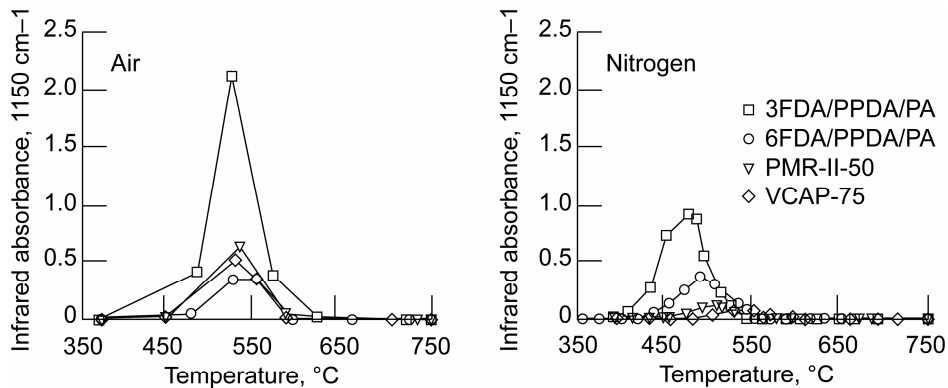

Figure 11.—Trifluoromethane evolution from various 3F and 6F based resins as determined via TGA/FTIR in air and nitrogen.

Our emphasis for continued 3F investigations shifted from the short term 316 to 371 °C aging to accelerated aging in order to simulate long term, lower temperature isothermal aging of 100,000 hr at 204 °C (400 °F) and 20,000 hr at 260 °C, needed for applications such as High Speed Civil Transport (HSCT) and Advanced Subsonic Engine Technology (AST). The resins were formulated in monomer combinations that would provide a slightly lower Tg for the lower temperature applications and a wide range of total material costs determined by the use inexpensive nonfluorinated BTDA or ODPA with 3FDAM (lowest cost combination) to 6FDAM (higher cost combination), or the use of 3F or 6F in either or both the dianhydride and diamine (very highest cost combinations). Figure 12 shows that the accelerated aging at 316 °C (600 °F) of both nonfluorinated BTDA or ODPA resins provides higher weight loss than for either fluorinated 3FDA or 6FDA resins. Figure 12 also shows that, with any of the dianhydrides, the 3FDAM weight loss always exceeded 6FDAM. Clearly, the earlier trend of 3F linkages providing higher weight loss is true for both the diamine, (fig. 12), and the dianhydride, (figs. 10 and 12).
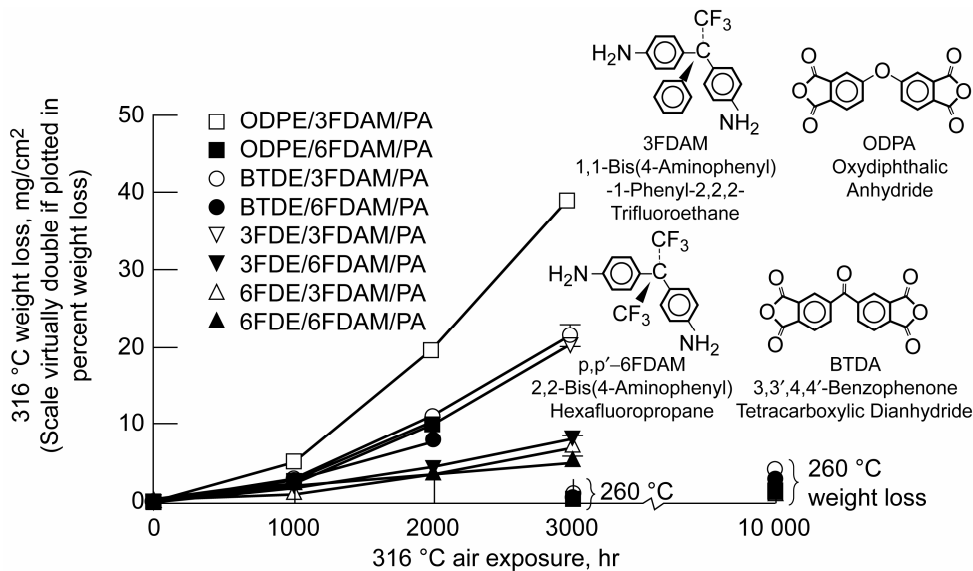
Figure 12.—Isothermal weight losses at 260 °C and 316 °C (500 and 600 °F) of 3FDAM and 6FDAM polyimides with various dianhydrides.
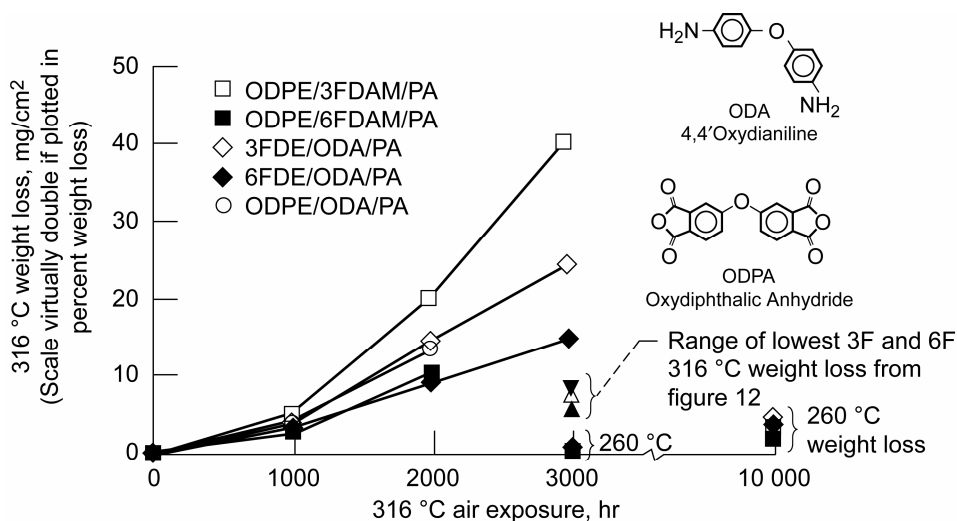
Figure 13.—316 °C (600 °F) weight losses of ether linkage based PA capped polyimides.

In fact, *the data very clearly shows that the more 3F, the higher the weight loss,* i.e., 6F used in both monomers = lowest loss, 3F used in either monomer = intermediate loss, while 3F used in both monomers = highest loss. However, figures 10 and 12 also show that when the aging temperature is lowered to 260 °C (500 °F), the differences in 3F versus 6F weight losses become quite small, but still real. It is important to note, however, that when either 3F or 6F linkages are replaced in either monomer by ether linkages, the rate of weight loss invariably increases (fig. 13). This clearly means the use of 3F is the next best thing to 6F for stability in aromatic condensation type resins even though 3F has poorer TOS than 6F. However, 3F can compensate for its poorer TOS with its increased synthetic versatility, increased reactivity (particularly in the diamine,[1, 14–15] but also somewhat in the dianhydride)[14–15] and lower monomer cost. This combined with the fact that 3F composite mechanical properties (some shown later in section 3.1.5) are similar to those of 6F thermoplastics (but less than comparable thermosets), demonstrates some potential to use 3F in polyimides for long term, lower temperature applications still exists. Unfortunately, recently both the HSCT and AST programs have been terminated. With the TOS of

3F clearly inferior to 6F for prolonged intermediate-to-high temperature exposure, our interest in 3F polyimides for high temperature jet engine and intermediate temperature structural applications also ceased.

3.1.4 Resin Remelt Viscosity

In a preliminary study of resin melt viscosity, various combinations of BTDA, ODPA, 3FDA, and 6FDA were imidized with 3FDAM, 6FDAM, and ODA using PA as the endcap to limit the molecular weight to a maximum 60,000 FMW as described in section 2.2. These molding powders were processed between a parallel plate rheometric fixture and their comparative remelt viscosities measured (fig. 14). Although this does not indicate the initial processing viscosity, the technique does indicate the final maximum processing viscosity because stable thermoplastics should not advance further in molecular weight, thus providing constant viscosity once processed. A stable remelt viscosity for thermoplastics could be useful in refabricating components or plastics that gave less than a satisfactory result on the initial processing attempt. The results show that all the fluorinated linkage combinations provide roughly a comparable remelt viscosity with a minimum around 420 °C. Interestingly, in comparing the minimum viscosity of 3F versus 6F, a slight trend toward lower viscosity of 6F linkages (either in only one or both monomers) can be visualized, i.e., using 6F in both linkages resulted in the lowest remelt viscosity range, while using 3F in both monomers resulted in the highest remelt viscosity, and combinations of 3F and 6F resulted in intermediate viscosities. However, using BTDE, instead of 3FDE or 6FDE, further raised the remelt viscosity by at least an order of magnitude.

Conversely, this increase was not true for the use of ether linkages. Use of ODPE or ODA in place of the corresponding 3F or 6F monomers is shown in figure 15. All combinations of 3F or 6F with an ether linkage replacing a fluorinated linkage continued to provide roughly similar remelt viscosity with its minimum still about 420 °C. Again, those combinations with the 6F linkage provided a slightly lower remelt viscosity than analogous 3F polyimides, e.g., 6FDE/ODA < 3FDE/ODA. Without any 3F or 6F linkage present, as in ODPE/ODA, the remelt viscosity was raised by as much as an order of magnitude (just as BTDE did when used with a fluorinated diamine). The 3F or 6F combinations, with or without an ether linkage present, were examined for intermediate term remelt viscosity stability by letting the rheometrics parallel plates experience three, 1 hr temperature holds at 360, 380, and 420 °C before stopping at 440 °C as shown in figure 16. As expected, because these were thermoplastics, the remelt
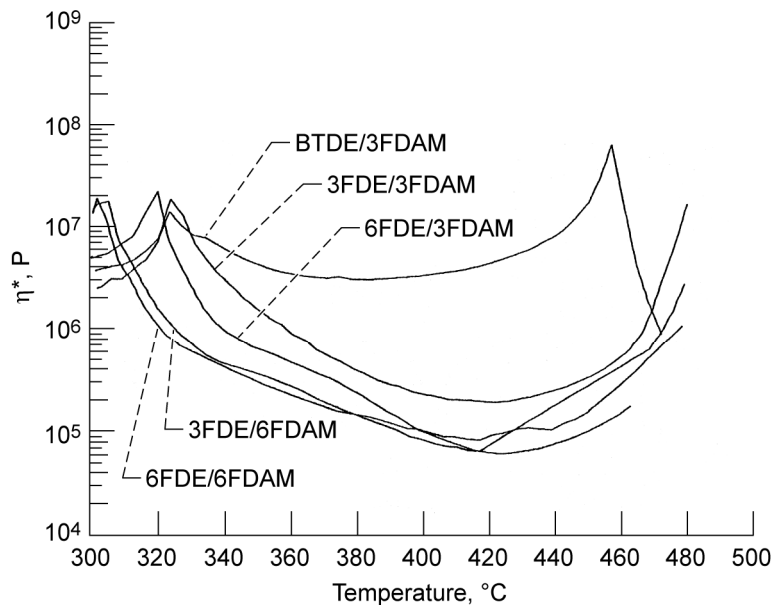
Figure 14.—Remelt viscosity of wholly 3F/6F linked polyimides versus carbonyl/3F linked polyimide.
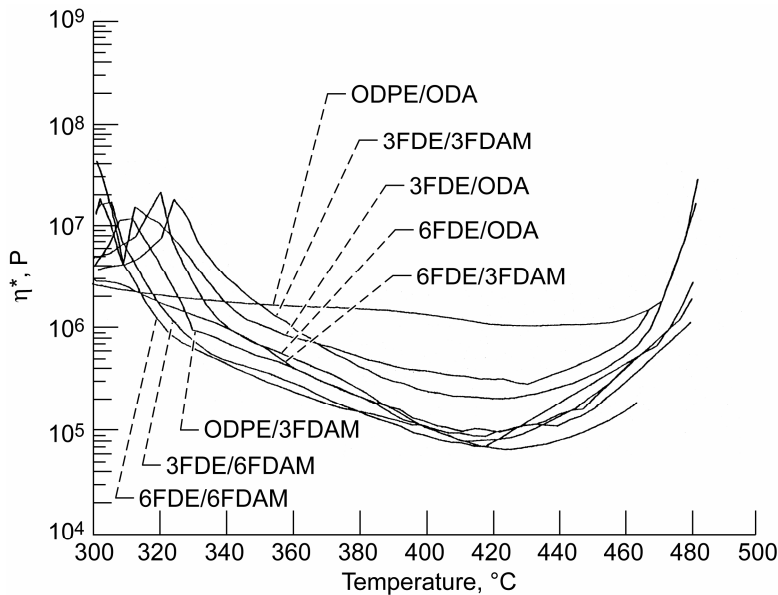
Figure 15.—Remelt viscosity of wholly 3F/6F linked polyimides versus ether/3F and ether/ether linked polyimides.
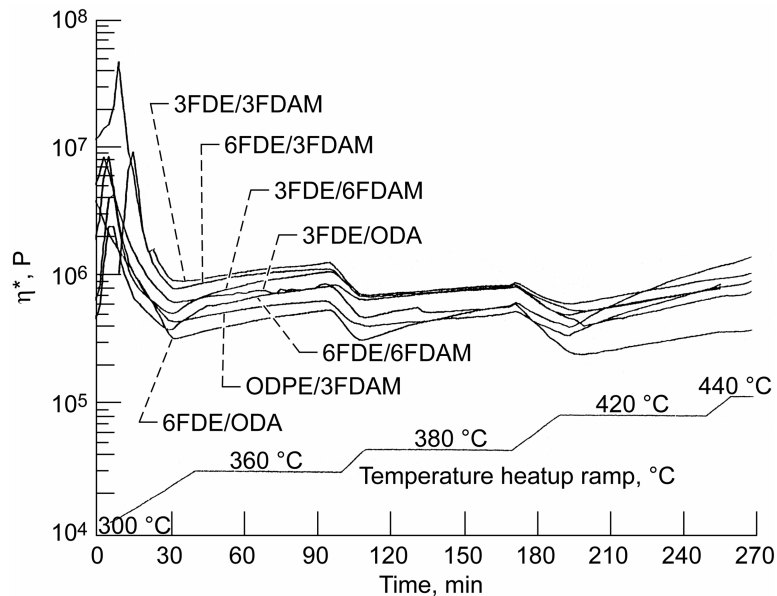
Figure 16.—Remelt viscosity after prolonged heating of 3F/6F linked and ether/3F linked polyimides.

viscosity did not significantly increase during these temperature holds, instead staying almost level within each temperature hold and decreasing slightly at each temperature ramp increase (fig. 16). This indicates the FMW seems to level off, even though the temperature holds were kept above the Tg to insure some mobility for any possible molecular weight advancement during the extended heating times. As in figures 14 and 15, there is a slight trend within the narrow viscosity range shown toward monomer combinations with 6F having lower remelt viscosity than those with 3F. A different study done by others will discuss in a later section (3.2.4) similar results of the initial melt (not remelt) viscosity of various 3F versus 6F polymer thermosets.

3.1.5 Composite Mechanical Properties

Tables 5 and 6 show the initial ILSS and FS of the PA capped thermoplastic resin combinations investigated; ODPA/ODA, ODPA/3FDAM, and 6FDA/3FDAM all formulated at 20, 40, and 60,000 calculated maximum FMW and processed as unidirectional G30–500 graphite fiber composites, as described in section 2.2. In tables 5 and 6, the mechanical properties of the two simulated autoclave processing cycles were averaged to form one column which still showed remarkable similarity of strengths when compared to the compression cycle results in the other column. More importantly, an inspection of both the initial and elevated temperature strengths shows that all the thermoplastics are around half the strength of what is obtained with the PMR polyimide thermosets that we currently use for aeronautical applications. Hence, additional data (long term composite TOS and retention of composite mechanical strengths) was not acquired. These composite mechanical results and the inferior TOS of 3F resins compared to 6F resins (section 3.1.3) led us to abandon the 3F thermoplastic approach, concluding the DARPA sponsored approach[13] using 3F SIPN (discussed later in sections 3.2.2 and 3.2.3) could potentially be more promising for our jet engine composite applications.

TABLE 5.—INTERLAMINAR SHEAR STRENGTH (ILSS) IN MPa OF UNIDIRECTIONAL
UNSIZED G30–500 GRAPHITE FIBER/POLYIMIDE COMPOSITES

Resin		ODPA/ODA/PA (lowest cost resin)		ODPA/3FDAM/PA (medium cost resin)		6FDA/3FDAM/PA (highest cost resin)	
		Cure Cycle		Cure Cycle		Cure Cycle	
		Compression	Vacuum bag	Compression	Vacuum bag	Compression	Vacuum bag
Molecular weight and Test temperature, °C							
20K	RT	70±4	64±10	43±2	41±2	29±0	31±4
20K	204	42±3	45±2	31±2	29±1	21±1	23±4
20K	260	5±1	5±1	16±4	16±3	14±1	17±3
40K	RT	51±4	56±1	51±2	47±4	39±7	45±8
40K	204	24±0	30±1	31±2	29±5	26±0	32±6
40K	260	8±0	11±1	23±0	28±3	35±1	23±2
60K	RT	19±2	37±7	37±4	37±3	36±6	34±2
60K	204	16±0	26±5	32±0	28±3	19±1	22±4
60K	260	5±0	9±4	20±1	21±2	15±1	18±1

Compression ILSS is average of two tests, autoclave ILSS is at least average of four tests, occasionally up to six tests.

TABLE 6.—FLEXURAL STRENGTH (FS) IN MPa OF UNIDIRECTIONAL
UNSIZED G30–500 GRAPHITE FIBER POLYIMIDE COMPOSITES

Resin		ODPA/ODA/PA (lowest cost resin)		ODPA/3FDAM/PA (medium cost resin)		6FDA/3FDAM/PA (highest cost resin)	
		Cure Cycle		Cure Cycle		Cure Cycle	
		Compression	Vacuum bag	Compression	Vacuum bag	Compression	Vacuum bag
Molecular weight and Test temperature, °C							
20K	RT	953±534	1059±319	890±33	662±167	449±2	480±223
20K	204	514±93	524±64	502±40	389±11	366±20	439±117
20K	260	46±4	46±4	204±28	184±46	191±3	224±64
40K	RT	825±323	1295±67	650±204	626±357	574±39	870±97
40K	204	532±58	603±89	303±87	384±83	459±7	631±81
40K	260	140±19	246±48	288±22	330±39	363±24	396±11
60K	RT	300±7	499±121	488±67	483±129	607±174	676±63
60K	204	213±4	359±48	253±50	315±70	422±64	380±85
60K	260	49±1	79±22	173±36	218±31	305±2	271±14

Compression FS is average of two tests, autoclave FS is at least average of four tests.

3.2 Thermoset 3F Addition Polyimides

The 3F based polyimide monomers have that been studied are 3FDAM[13, 17–20] and 3FDA[21–22, 35–36] in nadic,[17–22] ethynyl,[13] phenylethynyl,[13, 35–36] and vinyl (this paper) crosslinked polyimides as follows:

3.2.1 3FDAM Based Polyimides

Studies to replace MDA in PMR-15 with 3FDAM[17–20] have successfully produced composites with good initial mechanical properties and higher Tg, but then they failed more rapidly in ITA. Although the concept of using more oxidatively stable diamines, such as 3FDAM, to improve TOS sounds logical and desirable, the resultant TOS in ITA was dramatically poorer when 3FDAM was used to replace MDA in PMR-15. Instead, it appears that the combination of benzylics (MDA) and aliphatics (NE, nadic crosslink) in PMR-15 is responsible for the excellent surface char formation[17–20] that is, in turn, responsible for the superior TOS of PMR-15. Thus, the desirable synergistic effect of benzylic in combination with aliphatic was tampered with and lost by using a more oxidatively stable diamine, such as 3FDAM, to replace MDA, resulting in poorer TOS. This effect has been observed with many different diamines besides 3FDAM, and has been reported both in resin studies[17] and composite studies.[18–20]

Another study[13] using 3FDAM in thermosets also produced satisfactory processable composites by using Hercules IM7 graphite fiber prepregged with low molecular weight oligomers of BPDA/3FDAM endcapped with PA and PEA as a SIPN. Unfortunately, all evaluations stopped after demonstrating satisfactory composite processability. Thus, TOS data and composite mechanical property data is not available in reference 13. Also, the study initially used meta-aminophenyl acetylene (APA) as the crosslinker, but it reacted too rapidly at too low of a temperature to successfully process composites. Thus, reference 13 instead switched to the slower reacting PEA endcap as the crosslinker for preparation of the BPDA/3FDAM SIPN used in the thermoset composites.

3.2.2 3FDA Based Polyimides

3FDA has been studied in NE crosslinked resins[21–22] and composites[21] using both MDA[21] and PPDA[22] as the diamine. A back-to-back comparison against the corresponding 6F based systems was not done in either study so conclusions as to superior TOS, Tg or viscosity of 3F versus 6F could not be made. In fact, reference 22 only compared the TOS against a nonfluorinated PMR polyimide, BTDA/MDA/NE as PMR-30 and PMR-50, to conclude the 3F based PMR II-50 resin had better TOS at 371 °C than the BTDA/MDA analogs of PMR-30 and 50. However their[22] resin weight losses of 3F PMR II-50 (~10% at 100 hr and ~15% at 200 hr of 371 °C air aging) are in moderate agreement with our 3F PMR II-50 composite weight losses of 2 to 2.5% at 100 hr and > 6% at 200 hr after the composite weight losses are corrected by increasing 2.5 times to equal 5 to 7.5% at 100 hr and >15% at 200 hr to account for our 60/40 fiber/resin weight content. With that in mind, the only clear, definitive comparison of 3FDA versus 6FDA in crosslinked resins is our G40–600 and G40–700 carbon fiber composite data shown in figure 17. This figure again clearly shows 6F based polyimides have superior TOS to their 3F analogs as was seen for 3F thermoplastics (section 3.1.3). Additional support for poor 3F TOS is our 3F weight loss also agrees with other's[22] weight loss after again correcting for the fiber weight diluting the resin weight loss data.

3FDA has also been studied as a thermoset in other more recent studies[35–36] with a variety of diamines using PEA as the endcap. These studies are aimed toward low viscosity, fully imidized oligomers for coatings, rather than composites or TOS studies, so they are discussed later in section 3.2.4.
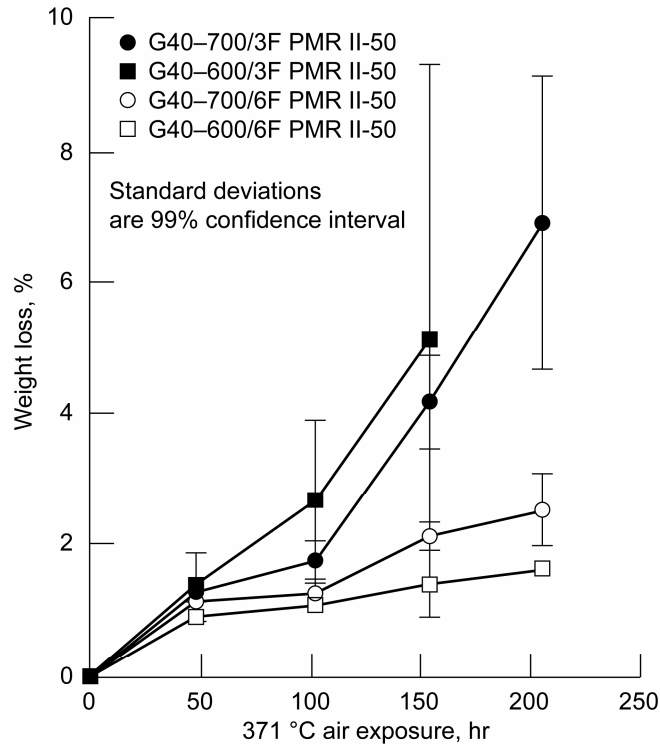
Figure 17.—Comparison of composite weight losses during
371 °C aging of 3F PMR II-50 versus 6F PMR II-50.

3.2.3 Composite Mechanical Properties

Compared to the extensive 3F thermoplastic properties in section 3.1.5, only limited composite mechanical property evaluations for the 3FDA and 3FDAM types of 3F thermosets (discussed in 3.2.1 and 3.2.2) are available. For composites containing 3FDAM, the BPDA/3FDAM/PEA and PA endcapped SIPN Hercules IM7 graphite fiber composites study[13] stopped after demonstrating composite processability, so composite mechanical properties were not determined. For the BTDA/3FDAM/NE study,[18, 20] an extensive set of composite mechanical properties are reported. These studies[18, 20] however also showed that while the initial room temperature and 316 °C ILSS, FS, and FM composite mechanical properties compared very favorably to those of PMR-15, the retention of these mechanical properties dropped rapidly because of the inferior TOS compared to PMR-15. This again was because the desirable synergistic benzylic-aliphatic surface char formation of PMR-15 was lost by replacing MDA with more oxidatively stable 3FDAM.[17–20]

For the composites containing 3FDA, reference 21 reported 3FDA/MDA/NE Celion 6000 graphite fiber composites had an initial room temperature ILSS of 23 MPa (3340 psi), an initial 316 °C ILSS of 23.9 MPa (3470 psi), and an initial 316 °C FS of 766 MPa (111,000 psi) with a corresponding FM of 137,300 MPa (19,900,000 psi) while not reporting any TOS or mechanicals after aging. A much more extensive set of 3FDA thermoset composite properties is shown in figures 18 to 20 for 3F PMR II-50/G40–600 and 700 graphite fiber composites compared to the analogous 6FDA composites. During the 200 hr of 371 °C aging, the mechanical properties of 3F versus 6F PMR II-50 remained remarkably comparable in spite of the poorer 3F TOS (section 3.2.2). The 371 °C ILSS (fig. 18) remained in the 20.7 to 27.6 MPa (3000 to 4000 psi) range for both 3F and 6F throughout the 371 °C aging. However, the room temperature FS (fig. 19) dropped from 1380 MPa (200,000 psi) to at least half that for 6F and almost one fourth that for 3F after the 200 hr 371 °C aging, while the related room temperature FM (fig. 20) also dropped from 138,000 MPa (20,000,000 psi) range to about half that for both 6F and 3F
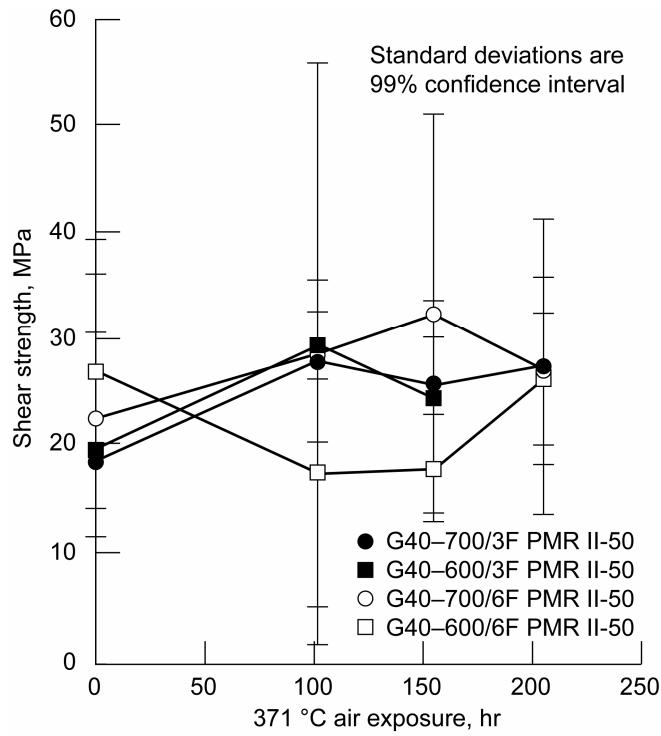
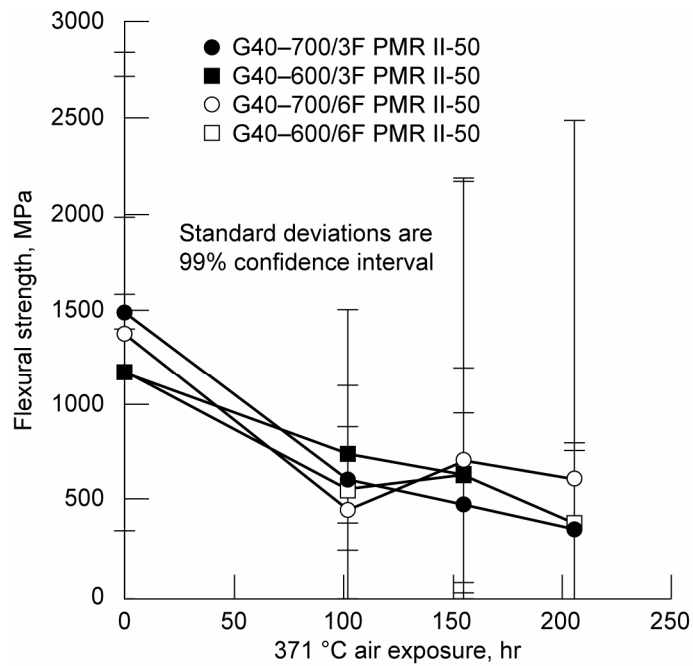Figure 18.—Retention of 371 °C ILSS during 200 hours of 371 °C aging of 3F versus 6F PMR II-50.

Figure 19.—Retention of room temperature FS during 200 hours of 371 °C aging of 3F versus 6F PMR II-50.
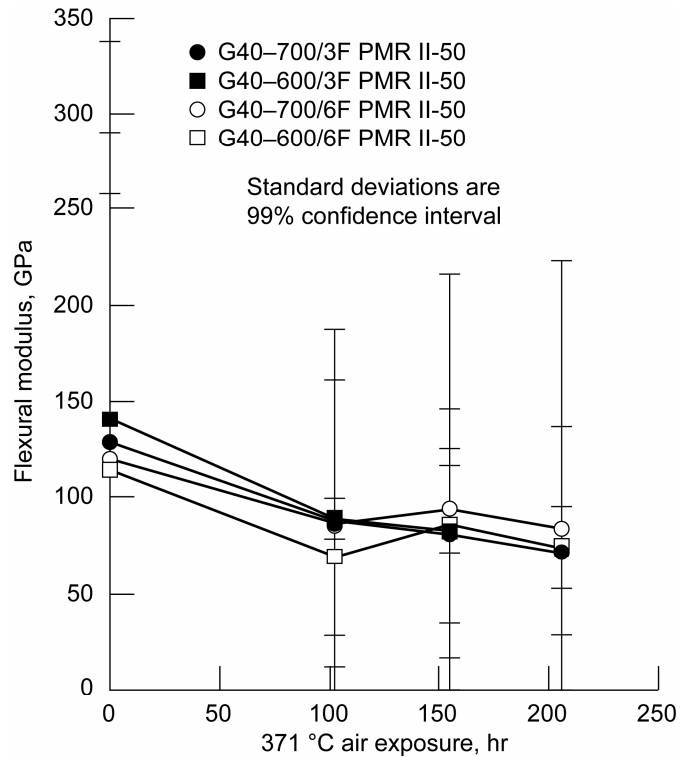
Figure 20.—Retention of room temperature FM during 200
hours of 371 °C aging of 3F versus 6F PMR II-50.

after the 200 hr 371 °C aging. In spite of similar property retention, the inferior 3F TOS, shown in figure 17, would clearly compromise dimensional stability sooner than in the 6F composites as 3F generated copious amounts of loose surface fiber during the aging, making 3F PMR II-50 clearly inferior to 6F PMR II-50.

3.2.4 Resin Processing Viscosity

There are many claims for low viscosity flow during processing of 3F polymers. However, direct comparisons of 3F versus 6F viscosities are scarce; found only in references 35 to 36 discussed in this section, in the remelt viscosity of 3F thermoplastic polyimides discussed in section 3.1.4, and outside the polyimide area in polyacrylates discussed in section 3.4.4. Low viscosity processing flow of thermoset 3F resins and composites using both 3FDAM[17–20] and 3FDA[21–22, 35] has been reported, but the claims are limited to 3F only, without any direct comparisons to analogous 6F polyimides. Reference 35 contains the most data as a comparative study of the processing viscosity of seven 3FDA polyimides, all at 5000 FMW, prepared with six different diamines (3,4'-ODA, 4,4'-ODA, PPDA, BDAF, 2,2'-bis (trifluoromethyl) benzidine (TFMB) and 1,3-bis (3-aminophenoxy) benzene (APB)) and an 85/15 mixture of 3,4'-ODA and APB (analogous to diamines used in the original phenyl ethynyl terminated imide (PETI) resin series). Figure 21 clearly shows the low processing viscosity from 275 to 370 °C of the seven 3FDA polyimide oligomers compared to the much higher viscosity of nonfluorinated BPDA in PETI-5. In addition, the initial viscosities of 3FDA resins remain low as reported in reference 35 during a 1 hr temperature hold at 310 °C, proving the 4-phenylethynyl phthalic anhydride (PEPA) endcap has not reacted extensively after 1 hr at 310 °C. An explanation based on the electron withdrawing power of 3F and 6F connecting linkages slowing the initiation of PEPA relative to BPDA is also presented in reference 35. The initial low viscosities and their stable isothermal viscosity are very desirable.
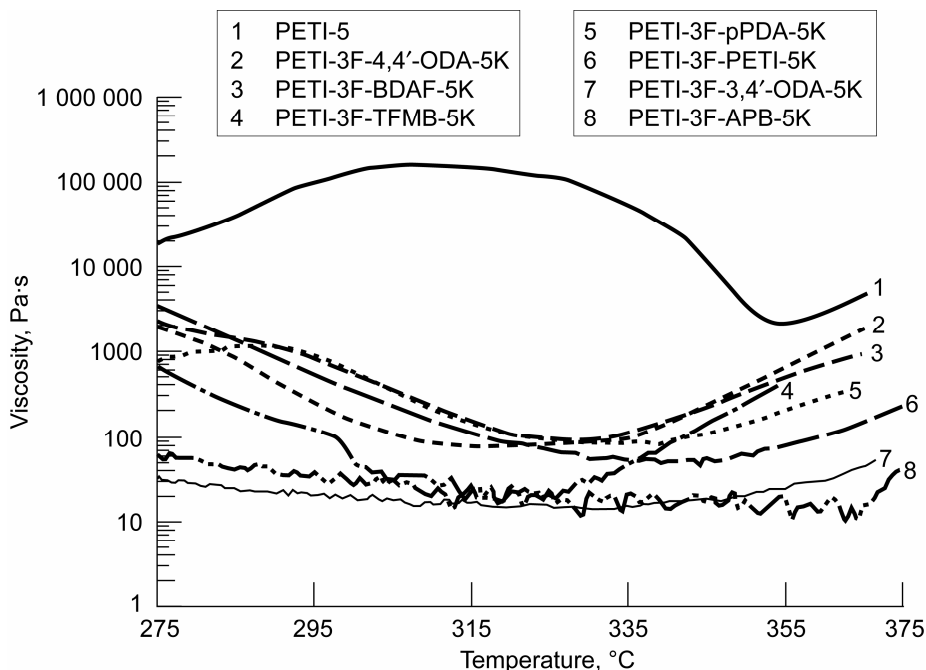
Figure 21.—Complex viscosity curves of PETI-3F 5000 FMW oligomides at 275-350 °C versus PETI-5.

Consequently, these resins are being studied[35] for melt coatings (on optical fibers), adhesives and resin transfer moldings (RTM).

The question as to which provides a lower melt viscosity, 3F or 6F, appears to remain unanswered, but swings toward 6F having a lower viscosity unless reactive 3F diluents are present. Reference 35 also contains a direct comparison of 3FDA versus 6FDA versus BPDA in PETI-3 and PETI-5 formulations. The data showed at 3000 FMW that 3F versus 6F were virtually identical (with BPDA considerably greater at both FMWs). The 3F versus 6F complex viscosity in Pascal sec.(at °C) was 27 versus 26 (at 290 °C), 17 versus 14 (at 300 °C), 7 versus 7 (at 310 °C) and 29 versus 16 (at 350 °C) with a minimum of 6 (at 314 °C) versus 3.5 (at 324 °C). However, at the higher 5000 FMW 3F complex viscosity was consistently higher than 6F as shown by 860 versus 255 (at 290 °C), 350 versus 129 (at 310 °C), 154 versus 77 (at 310 °C) and 65 versus 61 (at 350 °C) with a minimum of 59 (at 344 °C) versus 48 (at 337 °C). Both 3F and 6F PETI-3 and PETI-5 formulations had only minimal increases (almost doubling) in their initial viscosity after a 1 hr hold at 310 °C. Thus the low viscosity formulations have excellent potential for RTM resins. Reference 35 also included a discussion explaining the lower 3F viscosity (compared to 6FDA and BPDA) based on calculated solvent accessible surface area, molecular surface area and solvent excluded volume. However, as their data[35] showed, 3F was equal or higher than 6F. Thus, the meaning of their explanation is unclear.

Another direct comparison of 3F versus 6F processing viscosity was also recently published.[36] The study used 4000 and 7000 FMW oligomers of 80/20 and 70/30 PPDA/MPDA mixtures imidized with 3FDA and 6FDA. These were endcapped with PEPA for oligomer molecular weight control and crosslinking. The study was done with and without 10 and 20 mole percent additions of n = 1 reactive diluents, 3FDA and 6FDA/MPDA/PEPA, in order to study processing viscosity versus temperature. Using these four oligomers and two reactive diluents (which were all formed in N-methyl-2-pyrrollidinone (NMP) and isolated by precipitation into methanol), the study found the opposite result of reference 35. Now the minimum complex viscosity of the 3F polyimide was as much as an order of magnitude lower than 6F. In addition, the viscosity minimum occurred about 20 °C lower than the analogous 6F polyimide. The study[36] reported the 3F versus 6FDA/80/20 PPDA/MPDA/PEPA 4000

FMW oligomers, without any reactive diluents added, had a minimum complex viscosity/temperature in Pascal sec (at °C) as 419 (at 324 °C) versus 4442 (at 342 °C). When 20 mole percent 3F or 6FDA/MPDA/PEPA reactive diluents were added to the respective 3F or 6F FMW 4000 resin, the corresponding minimum complex viscosities were significantly lowered to 68 (at 325 °C) versus 1583 (at 347 °C) for 3F versus 6F resins.

Interestingly, the lower 3F processing viscosity result when using reactive diluents is the reverse of the 3F versus 6F polyimide remelt viscosity data discussed in section 3.1.4, the reverse of the 3F versus 6F polyacyrlate viscosity data discussed in section 3.4.4, and also the reverse of their own data in reference 35. Obviously, any general conclusion as to which has lower viscosity, 3F or 6F, has to be made within comparable polymer types and at comparable extents of cure and oligomer weights. The contradictory conclusions in both references 35 and 36 and in all three sections could be valid but specific to polymer types (imides or acrylates), polyimide type (diamines used), state of cure (crosslinkable oligomer or thermoplastic), solvent used and solvent residue (methanol or NMP), use of reactive diluents and/or resulting molecular weight (crosslinked or above Tg). In summary of this data, 6F consistently had lower or equal melt viscosity (depending on initial FMW) than 3F in all resin types studied, except for the 4000 FMW 3FDA/80/20 PPDA/MPDA/PEPA oligomers in reference 36 when used both with and without 20 mole percent of n = 1 3FDA/MPDA/PEPA reactive diluents.

3.3 Substituted, Functionalized, Pendant, and Modified 3F Polyimides

Historically, di- and tri- substituted 3F compounds were first extensively reported in the original 3F paper[11] and most were subsequently patented.[37] Interestingly, the patent listed the NASA Administrator at that time as an inventor in order to make the assignment to the U.S. government. In the patent examples,[37] 3F was incorporated into a variety of substituted bis (4-methyl, 4-methoxy, 4-hydroxy, 4-hydroxy-3-nitro, 4-phenoxy, 4-tert-butyl, 4-ethyl, 4-isopropyl, 4-fluoro, and 4-bromo) phenyl and tris (4-methyl, 4-carboxy, 4-formyl, and 4-methoxy) phenyl substituted 1,1,1-triphenyl-2,2,2-trifluoroethane compounds. The paper[11] and subsequent NASA Tech Brief[38] also reported bis- and tris- 4-amino, 4-acetamido, and 4-cyano substituted 3F compounds besides those in the patent.[37] However, they were unable to get the 1,1-bis(4-aminophenyl)-1-phenyl-2,2,2-trifluoroethane (3FDAM) composition of matter and process synthesis allowed for a U.S. patent. Thus, 3FDAM has been in the public domain ever since. For their purposes, these 3F compounds were the product of an organic synthesis project rather than an end result aimed at later specific polymers research by them. However, their patent,[37] paper,[11] and the NASA Tech Brief[38] followed by our seminal publication[1] which invented 3FDA and used 3FDA and 3FDAM in condensation polyimides, laid the groundwork for the ensuing large volume of 3F monomer and 3F polymer papers reported in the 1990's.

3.3.1 Scope of Modification of 3F Monomers and 3F Polyimides

The scope of the monomer/polymer applications of 3F resins is limited by only being able to withstand short term, high temperature exposure (such as in microelectronics manufacturing) or at best only withstanding prolonged intermediate temperatures. However, this is compensated for by the potential benefits that could lead to specific applications and improvements over 6F based resins, such as in the following areas:

1. A lower use temperature, lower cost alternative to the more expensive specialty 6F based resins commercially available, due to the lower cost TFA starting materials, the 3FDAM one step synthesis route and the improved 3FDAM polymerizability.

2. A technology for new fluorinated polyimide as colorless, optically clear 3F film products[39] (6F resins are colorless but commercially unavailable as film). However, this paper shows in figures 6 to 8 that nonfilm, unpostcured 3F polyimides exhibit more color than 6F after thermal treatment due to the poorer 3F TOS; potentially negating 3F for colorless films.

3. An approach to introduce increased polymer solubility using 3F pendant groups, such as was demonstrated using 3FDA with TFMB.[40–41]

4. A new method to produce high Tg polyimide dielectrics and nanofoams, such as was discussed in sections 3.3.6 and 3.3.8, respectively.

5. An improvement over the existing 6F technology due to the wide synthetic versatility that uses the 3F phenyl ring as the site to introduce functional groups[1–7, 10–11, 42–47] which later are used to chemically modify polymer properties.[1,7,42–47]

The last of these uses and modifications, incorporation of a functional group unto the 3F pendant phenyl ring, is the most versatile method to modify 3F polymers for specialty applications. This is partially due to the potentially low cost of TFA as a monomer building block. TFA has been prepared inexpensively[12–13] by conversion of low cost trifluoroacetic acid to its acid chloride, followed by reaction with benzene to produce TFA. Unfortunately, only general nondocumented examples of introduction of a synthetic site into the 3F pendant phenyl can be found in the patent[10] literature. Of these specific patent examples, none of the substituted pendant phenyl 3F monomers in reference 10 have been reported elsewhere, thus probably not existing other than within the patent discussion section and subsequent claims of reference 10. Even without these patent claims, actual other examples of synthetic pathways illustrating 3F synthetic versatility are shown in figure 22, which outlines the scope of how the 3F monomer and polyimide modifications can be done. Pendant 3F modifications for nonpolyimide monomers/polymers are discussed later in sections 3.4.1, 3.4.2, and 3.4.5. The 3F polyimide monomer/polymer modifications are reported to be done in four different ways:

1. -Can Introduce a variety of Xs into TFA initially by using 3F Pendant Phenyl[1–7, 11, 42–48] or 3F Pendant Naphthyl[45–47] reacted with Aniline,[1–7, 11, 38] Substituted Anilines,[9, 49–52] Phenols[12, 37, 53–56] and Substituted Phenols[37, 54]

2. -Can Introduce X during[2–7, 11] or after[3–4, 42–44] Monomer Synthesis, such as by Nitration[2–7] or Halogenation[42–44]

3. -Can Convert X to Y after X is introduced in Monomer Synthesis, such as by Oxidation[11] or Hydrolysis[11]

4. -Can Change X to a Different Group by a Displacement Reaction during[2–7] or after Monomer[2–7, 42–44] or Polymer Synthesis[6] or during Crosslinking[42–44]
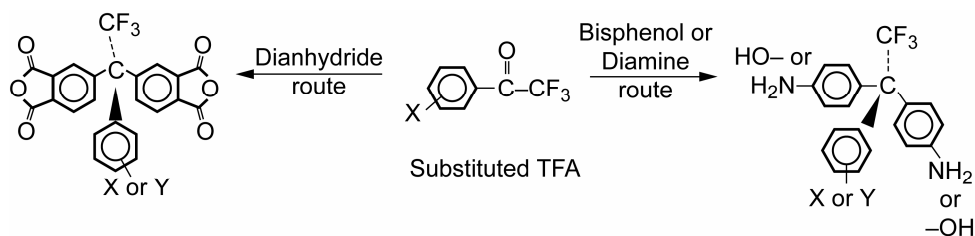

Figure 22.—Synthetic versatility of 3F technology to introduce other functional groups (X or Y) unto 3F pre-monomers, polyimide monomers and polyimides.

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3.3.2 Alkyl Substituted 3FDAM Monomers/Polyimides

Two alkyl substituted 3FDAM monomers have been prepared by us,[9, 49–50, 52] and two other alkyl substituted 3FDAM monomers have been prepared by others.[51, 57] These have all been accomplished using a route analogous to the original synthesis of 3FDAM[11] but replacing aniline with 2-methylaniline (o-toludine), 2,6-dimethylaniline, 2-methyl-6-*i*-propylaniline, and 2,6-di-*i*-propylaniline to produce the four substituted 3FDAMs in yields of 62, 26 to 64, 45, and 66%, respectively. In our studies, the resulting dimethyl and tetramethyl substituted 3FDAM monomers were polymerized with PMDA, BTDA, and 6FDA.[45, 49–50, 52] However, due to the low viscosity of the tetramethyl 3FDAM polyimides only the dimethyl 3FDAM made from o-toludine were successfully cast as films. These films were photolyzed with 350 nm ultraviolet (UV) light in order to examine their potential as photoresists by determining their Tg increase after UV exposure. The Tg shown in table 7 seemed to increase more from repeated thermal reruns in the TMA, rather than from the UV exposure. The lack of Tg advancement by UV light was perhaps due to the low strength of the UV light used. In either case, this concept of using an alkyl substituted diamine to advance the Tg for photoresist applications has been used with diamines[58] other than 3FDAM and, historically, was attempted to be commercialized by Ciba Geigy under the name Probimide 300®. However, the concept has had limited success in the microelectronics industry because the photospeed (photosensitivity to the UV = photoefficiency) dropped when used in polymers instead of model compounds. The advancement of Tg is reported to proceed by a cyclization mechanism involving the ortho alkyl group and the imide carbonyl.[59]

TABLE 7.—EFFECT OF UV LIGHT ON DIMETHYL 3FDAM IN BTDA, PMPA, AND 6FDA POLYIMIDES

DIANHYDRIDES	UV	GLASS TRANSITION TEMPERATURE, Tg, °C (FROM TMA)[a]					TGA PDT, °C
		RUN 1	RUN 2	RUN 3	RUN 4	RUN 5	
PMDA	BEFORE	321 (460)	387 (460)	—	—	—	555
	AFTER	324 (460)	360 (460)	398 (460)	—	—	555[b]
6FDA	BEFORE	308 (410)	325 (460)	—	—	—	543
	AFTER	290 (460)	308 (460)	320 (460)	360 (460)	380 (460)	555[b], 554[c]
BTDA	BEFORE	291 (400)	310 (460)	329 (460)	339 (460)	—	549
	AFTER	293 (400)	313 (460)	320 (460)	NONE (460)	NONE (460)	566[b], 567[c]

[a]Numbers in parentheses represent the maximum temperature attained in each rerun
[b]After 2-hr Exposure to 350 nm UV
[c]After UV exposure and then heat to 460 °C in TMA

Others[51, 57] have taken our Tg evaluation much further by using the methyl and isopropyl substituted 3FDAM monomers to prepare only 6FDA based substituted polyimides, followed by evaluation as gas separator membranes, both before and after UV exposure. Without UV exposure, their oxygen permeability, ($P\ O_2$), in Barrer units greatly increased to the 25 to 80 range compared to an unsubstituted 3FDAM permeability of almost 4, but their oxygen/nitrogen selectivity ratio, ($\alpha\ (O_2/N_2)$), dropped to 3 to 3.5 range compared to a selectivity of 5 for the unsubstituted 3FDAM, as seen in table 8. Thus, all of the substituted 3FDAM polyimdes showed greatly enhanced permeability while sacrificing some selectivity. The permeability and selectivity of ortho-substituted diamines in 6FDA polyimides was further investigated in a modification of this work[59] by using UV exposure at < 300 nm. In all the cases reported,[59] the greatly increased permeability from using ortho-alkylation decreased only slightly after UV exposure compared to the large increase initially observed by introducing alkylation. At the same time, the selectivity that had decreased significantly from using ortho alkyls increased back toward the initial permeability without alkylation present. For example, in table 8-example 3A[59], after UV exposure, the methyl isopropyl substituted 3FDAM permeability (example 3) only dropped from 50 (57.2 in

patent [51,57]) to 42 while the selectivity increased from 3.5 to 5.5; but, without any alkyl groups present, the permeability was much lower at 3.83, while the selectivity was comparable at 5.0. Thus the concept of using ortho alkylation in any diamine, with or without UV exposure, shows great promise of increased permeability while maintaining selectivity.

TABLE 8.—PERMEABILITY IN BARRER UNITS AND SELECTIVITY RATIO
OF UV UNEXPOSED 6FDA/ALKYL SUBSTITUTED 3FDAM POLYIMIDES
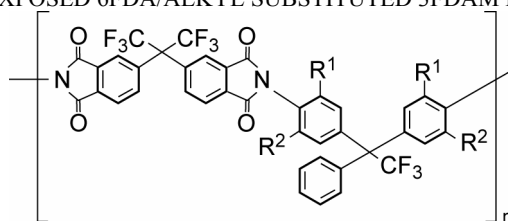
Example	R^1	R^2	$\bar{P}_{O_2}$	$\propto(O_2/N_2)$
1*	H	H	3.83	5.0
2	CH_3	CH_3	25.5	3.0
3	CH_3	$i\text{-}C_3H_7$	50 and 57.2	3.5
3A After UV Exposure	CH_3	$i\text{-}C_3H_7$	42	5.5
4	$i\text{-}C_3H_7$	$i\text{-}C_3H_7$	80.0	3.22

*Unsubstituted Comparative example

The use of 3F in the dianhydride, instead of the diamine, has also been investigated[60] in gas separator membranes using as nonalkylated diamines, MPDA, 1,5-diaminonaphthalene (DAN), and 3,3'-diaminobenzophenone (DAB), and using as ortho-alkylated diamines, 9,9-bis (3-methyl-4-aminophenyl) fluorene (BMAPF), 2,4,6-trimethyl meta-phenylenediamine (TMMPDA), and 9,9-bis (3,5-dimethyl-4-aminophenyl) fluorene (BDMAPF). The results shown in table 9 again clearly show that ortho-alkylation of the diamines greatly increases P O_2 while also lowering α (O_2/N_2), compared to the three nonalkylated diamines, as was seen also for the 6FDA polyimides in table 8. For example, MPDA versus TMMPDA had a 35 fold increase in P O_2 while only lowering α(O_2/N_2) by 40%. However, replacing 6FDA with 3FDA gave values for 3FDA/BDMAPF that are 40% lower permeability compared the analogous 6FDA polyimide, while the 3FDA selectivity showed only a 23% increase to 4.49. The lower P O_2 using 3FDA versus 6FDA clearly shows the increases in P O_2 in table 9, while maintaining or slightly increasing the α (O_2/N_2), is due to the use of ortho-alkylation, rather than the use 3F in either monomer, as the technique also works for non 3F diamines.[58–59] Thus, 3F technology is only the easy synthetic route to prepare the ortho-alkylated 3FDAM monomers. The lack of any technical advantage of 3FDA over 6FDA in this gas separator membrane preliminary study[60] discouraged further pursuit of 3FDA for gas separator applications, although gases other than O_2/N_2 have not been studied or reported.

TABLE 9.—PERMEABILITY IN BARRER UNITS AND SELECTIVITY RATIO
OF 3FDA POLYIMIDES CONTAINING VARIOUS UNSUBSTITUTED
AND ALKYL SUBSTITUTED AROMATIC DIAMINES

3FDA/Various Diamines	P (O_2)	$\propto (O_2/N_2)$
Unsubstituted Diamines		
MPDA	1.25	7.36
DAN	4.48	6.37
DAB	0.44	9.01
Substituted Diamines		
BMAPE	7.55	6.11
TMMPDA	43.8	4.43
BDMAPF	36.2	4.49
6FDA*/BDMAPF	60.1	3.63

*Comparative example from reference 53

3.3.3 Functionalized Pendant Ethynyl 3FDAM Monomers/Polyimides

Ethynyl substituted 3FDAM monomers have been prepared[42] in a three step procedure by the preparation of 4-bromo TFA or 4-iodo TFA, followed by reaction with aniline, and last, the conversion of the bromo group to ethynyl or hexylethynyl substitutents and the iodo group to phenylethynyl substitutent in overall yields of 53, 51, and 39%, respectively. This is, perhaps, the most elaborate example of the 3F pendant phenyl synthetic versatility. Initially the 3F substitution was introduced into the TFA starting material in order to synthesize pendant substituted 3FDAM monomer from pendant substituted TFA. This was followed by conversion of the pendant substituted 3FDAM monomer into three other pendant substituted 3FDAM monomers (EDA, HDA, and PEDA for ethynyl, hexylethynyl, and phenylethynyl 3FDAM monomers, respectively). Then, during polymerization, the new 3FDAM substitution site was used to crosslink the 3F polyimides in order to control and modify subsequent polymer properties. This covers the entire gambit of possible places/routes to use 3F technology in order to modify 3F materials as follows: in the starting TFA, after the 3F monomer is synthesized and during and/or after the polymerization of the 3F polymer, as illustrated in figure 22.

Using these three ethynyl substituted 3FDAMs, polyimides films were initially prepared[42] and patented[43] with BTDA and 6FDA. The emphasis then shifted to 6FDA copolyimides of all three ethynyl substituted 3FDAM monomers mixed with BDAF, while only EDA and PEDA were mixed with 3FDAM; all five at 10/90 mole percent ethynyl diamine/nonethynyl diamine content. The room temperature and 177 °C mechanical properties of the three 6FDA/ethynyl 3FDAM/BDAF copolyimides shown in table 10 demonstrate that ethynyl crosslinking drastically reduced the elongation while maintaining the tensile strength along with slight to excellent gains in tensile modulus.

TABLE 10.—TOS AND FILM ROOM TEMPERATURE AND 177 °C MECHANICAL
PROPERTIES OF 6FDA/ETHYNYL CROSSLINKED 3FDAM/BDAF COPOLYIMIDES

Diamine with BDAF	5% weight loss by TGA, °C		23 °C tensile properties (150 °C)		
	Air	N$_2$	Strength, MPa	Modulus, GPa	Elongation, %
10% EDA	468	493	102.0 (68.3)	2.87 (2.15)	6.7 (7.5)
10% HDA	401	493	122.7 (66.9)	3.68 (2.19)	5.9 (12.1)
10% PEDA	450	493	122.0 (66.2)	3.57 (2.08)	6.1 (47)
100% BDAF	—	—	107.6 (71.7)	2.99 (1.93)	26.7 (111)

3.3.4 Pendant Perfluoro Phenyl 3FDAM Monomers/Polyimides

The pendant phenyl site of TFA has also been used as the site for introducing five more fluorines beyond the three fluorines already in the 3F group.[48] This was done by condensing o-xylene with 2,3,4,5,6-pentafluoro-α,α,α-trifluoroacetophenone to produce the tetramethyl precursor to the 8F dianhydride (with eight fluorines on the connecting linkage group in a 30 to 40% yield. Oxidation was done by nitric acid, followed by dehydration to produce the perfluoro analog of 3FDA (8FDA). This new

dianhydride has been studied in polyimides prepared using PPDA, BDAF, meta-6FDAM, 3,4'-ODA and TFMB. The 8FDA/PPDA polymer showed slightly better dynamic TGA ($T_{d-5\% \text{ and } 10\%}$) in air and nitrogen, slightly higher char yield, but only comparable weight loss of 3.5% after 240 hr of 371 °C air exposure, with higher weight loss at 450 hr (6.3 versus 5.3%) when compared to commercially available 6FDA/PPDA (AVIMID N[®]). As expected, the 8FDA/PPDA also showed 20 to 30% lower moisture uptake after 24 hr at room temperature and a 19 to 24 percent density increase; both caused by the increased fluorine content present in 8FDA compared to the commercially available 6FDA/PPDA AVIMID N[®]. More importantly, the dielectric constant (DE) of the five 8FDA polyimides (in the diamine order listed above) was 26, 17, 2, 14, and 27% lower than the comparable 6FDA polyimide. The lower DE with increasing fluorine content trend is well documented in polyimides used in the microelectronic industry, as illustrated later in section 3.3.6. Because the 8FDA polyimides' TOS appears somewhat better during ITA than the 3FDA polyimide ITA TOS reported in this paper, the 8FDA polyimides could be viable candidates for many electronic and high temperature applications, only perhaps currently limited by a comprehensive Tg study of the 8FDA polyimides and an improved 8FDA synthesis path of lower monomer cost.

3.3.5 *Pendant Phenyl, Pendant Phenoxy, and Naphthyl Modified 3FDAM Monomers/Polyimides*

The pendant phenyl site of TFA has also been used as a site to introduce pendant 4-phenyl and 4-phenoxy groups starting from 4-phenyl TFA and 4-phenoxy TFA and to introduce a 2-naphthyl group by replacing TFA with α,α,α-trifluoro-2-acetylnaphthalene in order to synthesize pendant and modified 3FDAMs.[45–47] The α,α,α-trifluoroaryl ketone synthesis was in 60, 51, and 47% yields, respectively.[46–47] These were converted to their respective 3FDAMs in 21, 17, and 12% yields.[47] However, starting from α,α,α-trifluoro-1-acetylnaphthalene did not produce a naphthyl-modified 3FDAM.[45] Instead, it gave an imine product, probably due to steric congestions at the 1-naphthyl peri position. The 4-phenyl and 4-phenoxy pendant substituted 3FDAMs were polymerized with PMDA using PA endcap in a traditional solution condensation polymerization technique, providing inherent viscosities of 0.46 and 0.48. The $T_{d's}$ were 511 and 490 °C while the Tg's were 411 and 360 °C, respectively.[46–47] The 2-naphthyl modified 3FDAM was not examined in polyimides.

3.3.6 *Xanthene Modified 3FDA Monomers/Polyimides*

Additional polyimide rigidity was introduced by the use of two xanthene modified 3F type dianhydrides in order to raise the Tg while maintaining high TOS, low moisture uptake, low linear coefficient of thermal expansion (CTE), low DE, good polymer solubility and the good processing flow needed for film formation in microelectronic applications. The first xanthene modified 3FDA (3FCDA) was synthesized[61–62] by an 8 hr 120 °C cyclobridging reaction of TFA with 2,3,6,7-tetramethyl diphenylether (dixylyl ether, DXE) in 80 to 90% yields followed by oxidation to 3FCDA in 76% yield. The patent[63] reported that the yield increased to 92% for a six fold larger reaction when done at 130 °C for 8 hr, but at 140 °C the yield dropped to 58%. The second xanthene modified 3FDA (3FPXPXDA) was synthesized[64] as a mixture of two isomers from the two cyclobridging ring closures by the reaction of TFA with 1,3-bis (3,4-dimethylphenoxy) benzene (BDMPB) in 50% yield followed by oxidation to the doubly bridged 3FPXPXDA in a high but unreported yield. The two 3FPXPXDA isomers were separable by successive recrystallizations but used as a mixture for polymerizations. The two 3F xanthene modified dianhydride synthesis routes are shown in figure 23.

The 6F analog, 6FCDA, was also prepared by the cyclobridging DXE route in a much lower 33 to 41% yield[62] (or patent[63] yield = 29 to 32%), followed by permanganate oxidation and dehydration to the dianhydride in a 60 to 95% yield (or patent[63] yield = 61%). However, when 6FCDA precursor was synthesized by a one step condensation route of 3,4-dimethylphenol (DMP) forming DXE at the same time that DMP and the resulting DXE condensed with HFA, or HFPO, an even lower yield of 17% resulted.[62–63] Obviously, these competing condensation reactions can also yield additional side products
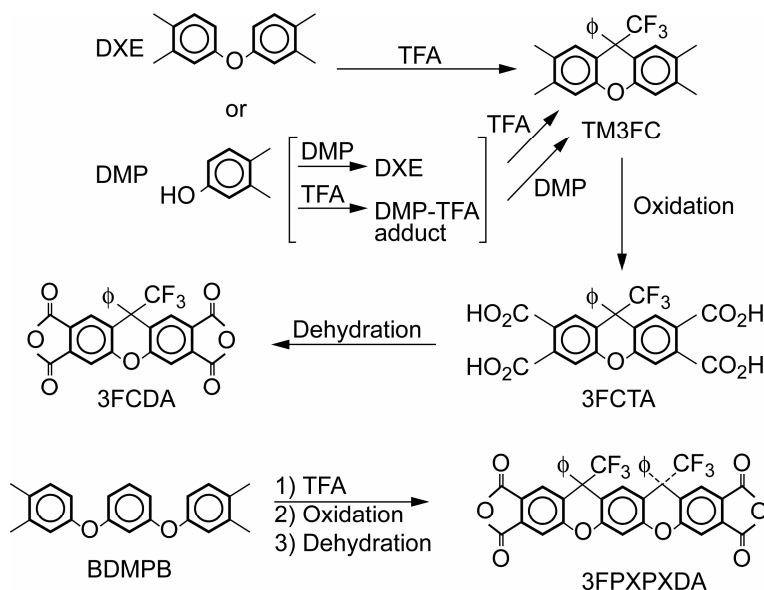
Figure 23.—Synthesis routes to 3F xanthene type dianhydrides.

because the TFA and HFA condensations can also proceed ortho to the hydroxyl next to the meta DMP methyl, rather than ortho to the hydroxyl but not next to a methyl of DMP, when using condensations starting from DMP instead of DXE. This DMP pathway was not investigated using TFA, as the cyclobridging DXE pathway was already far superior with 80 to 92% yields compared to the troublesome low yield condensation pathway when using HFA. This success reflects very highly on the versatility of 3F synthesis capabilities. When the condensation path instead followed the cyclobridging pathway starting from DXE, instead of DMP, other tetramethyl substitutions could also result from DXE condensing with two HFAs or TFAs, thus competing with the cyclobridging reaction. This route was also more troublesome using HFA, rather than using TFA, as seen in the lower yields of 29 to 41% for 6F versus 80 to 92% for the superior 3F technology. The same was also true when DXE was replaced with 4,4'-ditolyl ether (DTE) in the synthesis route of analogous xanthene diacids. The yield was only 7% for the cyclobridging with HFA versus 73% for TFA,[62–63] again clearly attesting to the superior synthetic capabilities of 3F chemistry.

A direct variation on this 3F technology was also reported by reacting meta-trifluoromethyl TFA with DXE to provide the corresponding tetramethyl 3F precursor in a 33% yield, but the dianhydride oxidation product was only illustrated, not reported,[62] in the experimental section. The synthesis of twelve additional rigid dianhydrides,[62–63,65] some quite similar to 3FDA, have also been reported by this xanthene condensation route as follows: using other fluorinated aryl ketones than TFA (perfluoro ethyl, propyl, and octyl groups in place of trifluoromethyl groups within TFA and also 4-perfluorohexyl phenyl heptafluoro-1-butanone), using nonfluorinated aryl ketones (benzophenone and acetophenone) and even using nonaryl ketones (1,1,1-trifluoroacetone, perfluoro-2-butanone, acetone, 3-pentanone, cyclopentanone, and cyclohexanone), all in place of using TFA. The wide variety of modified 3F linkages formed reflects very highly on the versatility of 3F synthetic technology.

The synthetic versatility compliments the main reason for incorporating 3F technology into xanthene ring structures, the initial reason being to make rigid planar dianhydrides for low DE and high Tg desired by the microelectronic industry. Interestingly, only some of these goals were met with the 3FCDA xanthene ring structure, as it was shown to be nonplanar. Using the bistolyl imide derivative of 3FCDA for x-ray analysis, the xanthane ring was shown to be tilted by 10° toward the oxygen bridge, but along with a 21 to 22° angle across the xanthene ring, like a butterfly wings along the molecule's length.[62, 66] The cresent shape in xanthene diahydrides is as due to the difference in the longer carbon-carbon bond

length versus the shorter carbon-oxygen bond length in the xanthene ring. Using the tetramethyl 6FCDA precursor, the same cresent shape result, but now planar, was found for the 6F analog, as seen by the butterfly angle at the xanthene ring was now absent in the x-ray analysis. This suggests the larger 3F group at the xanthene ring causes the 21 to 22° angle butterfly fold. Reference 65 reported that the nature of the substitutents determined the size of the butterfly angle, with symmetric groups being required for planarity, but as size increased, even symmetry could not cause planarity, as with both groups being phenyls a 31° butterfly angle resulted.

The two 3F xanthene type dianhydrides, 3FCDA and 3FPXPXDA have been prepared in traditional solution condensation polymerizations with many diamines.[65–73] The 3FCDA has been polymerized with ODA,[65–67] TFMB,[65–70] (3,4'-ODA, MPDA, PPDA, 6FDAM, DAN, diaminodurene (DAD)),[66–67] (3,5-diaminobenzotrifluoride (DABTF), 2,5-dimethyl-1,4-PPDA (DMPPDA), 2-chloro-5-methyl-PPDA (CMPPDA) and 3,3',5,5'-tetramethylbenzidine (TMB)),[66] 2,2'-dimethylbenzidine (DMB),[67] (2,2'-trifluoromethoxybenzidine (TFMOB), and 2,2'-tetrafluoroethoxybenzidine (TFEOB)).[68–69] The 3CFDA/TFMB polyimide has also been patented.[70] This extensive list of 3FCDA polyimides was characterized to show which polyimides exhibited the desirable low DE, low CTE, high TOS, high Tg, high molecular weights, low moisture uptake, good polymer solubility, good film quality and good film mechanical properties. Generally, the use of 3FCDA versus 3FDA raised Tg, lowered CTE and improved polymer solubility while maintaining TOS, DE, film quality and mechanical properties, as extensively discussed in references 65 to 69. The well known relationship of low fluorine content to low DE and low moisture uptake was also shown for the extensive list of polyimides in reference 67. Besides these polyimides, 3FCDA polyimides have been modified with pendant groups (by means other than using 3F technology to introduce the pendant groups on the 3F phenyl site as shown in Figure 22), done by introducing 2,2-trifluoromethyl-2-heptafluoropropyl-1-ethane groups in the meta position on MPDA.[71] This modified 3FCDA polyimide and its 6FCDA analog, along with a 6FDA control comparison polyimide, were all soluble polyimides with good film forming properties, desired because the resulting increased fluorine content is part of the continued quest for lower DE of polyimides for microelectronics applications. The 3FCDA and 6FCDA polyimides had comparable tensile strength (TS), elongation (E), tensile modulus (TM), CTE, DE, and TGA-$T_{d-5\% \text{ loss}}$. However, the 6FCDA had lower moisture uptake (0.06 versus 0.11%), probably due to the higher fluorine content in 6FCDA versus 3FCDA. The control 6FDA polyimide compared somewhat favorably, but only had about one-half the TS, one-fifth the E, three fourths the TM and 40% higher CTE compared to the 3F and 6FCDA polyimides.[71] Another modified 3FCDA polyimide has also been prepared using poly (propylene oxide) grafts as endcaps when copolymerized with 3FDAM/3FCDA polyimides.[72] The poly (propylene oxide) endcapped 3FCDA polymers will be discussed later in the polyimide nanofoam section 3.3.8 along with PMDA/3FDAM nanofoams.

The even more rigid and longer 3FPXPXDA, compared to 3CFDA, has also been polymerized using traditional solution condensation polymerization techniques with ODA, PPDA, DAD, and TFMB.[64, 73] The polyimides all formed good films except PPDA. The other three polymers exhibited low DE, high Tg, high TOS, low CTE (except ODA) and good polymer solubility.

3.3.7 3F-BDAF Monomers/Polyimides

Two synthetic routes have been used to prepare the 3F analog to 6F based BDAF. The first is analogous to the BDAF synthesis using a traditional three-step pathway[53] starting from TFA; formation of the 3F bisphenol (3FBP),[12, 37, 53–56] followed by reaction with p-fluoronitrobenzene and, last, catalytic hydrogenation to produce 3FBDAF in a 74% overall yield. Later, the route was changed to a two-step pathway[74–75] of reacting TFA with 4-nitrophenyl phenyl ether, followed by catalytic reduction to produce the 3F analog of BDAF in a 72% overall yield (but the overall yield would have been 82% had the identical 3F dinitro precursor reduced in the 91% yield obtained in the earlier three-step route).[53] A comparison of these routes is shown in figure 24. The multiple routes further demonstrate the versatility of 3F synthesis capability.
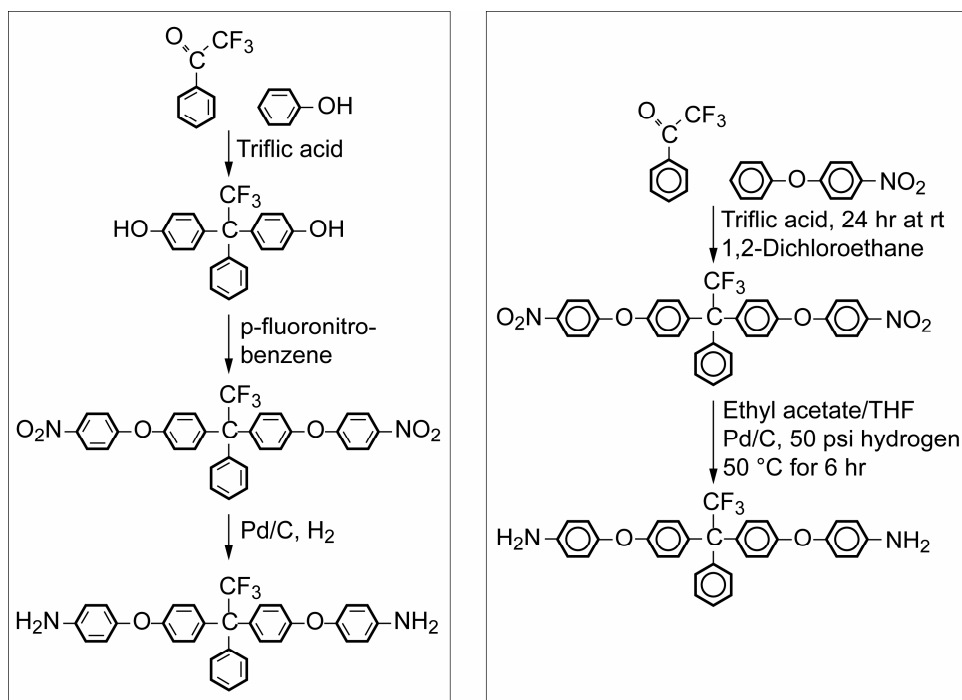
Figure 24.—Synthesis routes to 3FBDAF monomer.

The 3FBDAF monomer has been polymerized with PMDA, BPDA, 6FDA, and also PMDA/6FDA mixtures to produce polyimides and copolyimide films[74–75] using PA endcaps to control the molecular weights. The PMDA/3FBDAF polyimide was semicrystalline and had identical Tg to the 6F analog. The copolyimides made by introducing 6FDA into the PMDA/3FBDAF polyimides made the copolyimide meltable but also destroyed the semicrystalline nature.

3.3.8 3FDAM Polyimide Nanofoam Modifications

PMDA/3FDAM polyimides have been modified for examination as nanofoams, desired for lower DE in microelectronic applications. The modifications were done by introducing aliphatic sites and aliphatic polymers onto the PMDA/3FDAM polyimides by the use of blocks of poly (α-methyl styrene),[76] poly (caprolactone),[77] poly (propylene oxide)[78] and by grafted poly (propylene oxide)[79] as shown in figure 25. PMDA/mixed 3FDAM and pendant ethynyl 3FDAM polyimides (for use as a crosslinking site to strengthen the nanofoam) have also been prepared using poly (α-methyl styrene) as the foaming agent for when it depolymerizes and volatilizes.[80] 3FCDA/3FDAM polyimides have also been modified by the poly (propylene oxide) route,[72] while 3FCDA/MPDA polyimides have been modified by incorporating 2,2-trifluoromethyl-2-heptafluoropropyl-1-ethane pendant groups on MPDA.[71] However, none of these were modified by 3F synthesis technology; rather, changes were introduced as copolymer blocks, grafts, pendants, and endcaps, just as had been done for the non 3F polyimide nanofoam technology. The nanofoam concept in these cases is to depolymerize or pyrolyze the aliphatics in order to create gaseous nano-voids which lower the DE of the polyimide film, (the DE of air being one in order to dilute the higher DE of the polyimide). The challenge with this concept has been to produce uniform size and distribution of the nano-voids for maximum lowering of the DE. Toward addressing the uniformity problem, nanofoams of the PMDA/3FDAM polyimides have been analyzed using transmission electron microscopy (TEM),[76, 78, 80–82] microdeformation of their thin films[83] and small angle x-ray scattering (SAXS).[77, 79] An extensive review of the nanofoam area, including 3F polyimdes, was recently published as reference 84.

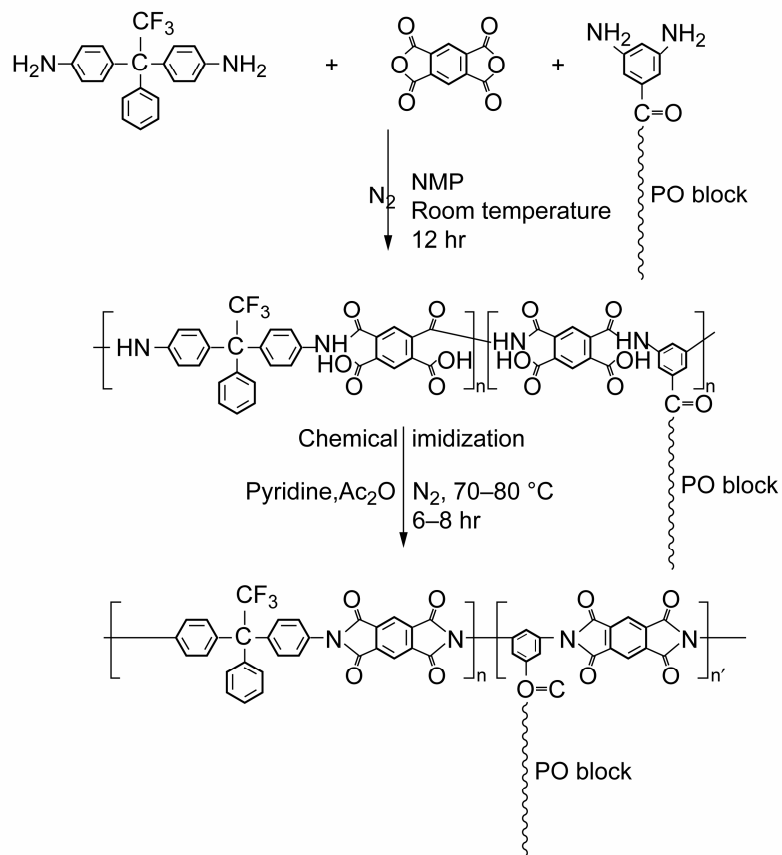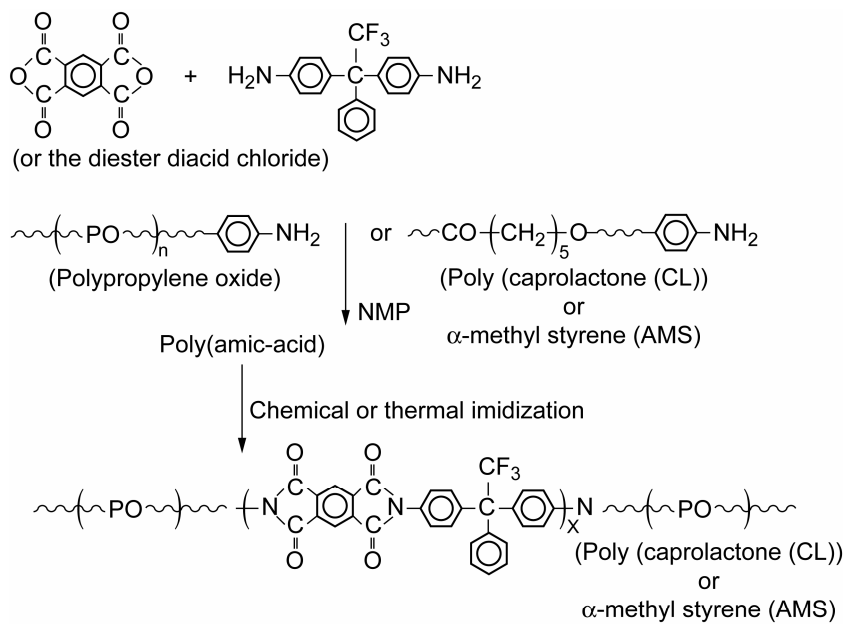Figure 25.—Representative synthetic pathways to PMDA/3FDAM nanofoams.

3.4 Advanced 3F Polymers Other Than 3F Polyimides

The wide range of 3F compounds already synthesized (section 3.3) clearly demonstrates that the synthetic versatility already exists for introducing 3F into many other types of new monomers/polymers analogous to the existing wide spectrum of 6F monomers/polymers. The synthetic 3F building blocks starting from TFA[12–13] are represented by the 3F dicarboxylic acid (3FDCA),[11] 3FDAM,[1–7, 11, 38] 3FDA,[1–10] and 3F bisphenol (3FBP)[12, 37, 53–56] starting monomers already known. Their existence only awaits the expanded use for 3F monomers and modified 3F monomers into advanced 3F polymers (other than polyimides). The following sections detail the incorporation of 3F into advanced 3F monomers/polymers other than for 3F polyimides.

3.4.1 Scope of 3F Monomers Known for Other 3F Polymer Types

Similar to the synthesis of pendant substituted polyimide monomers, 3F synthesis technology can be further expanded so the 3F building block (TFA) can start from substituted benzenes to produce substituted TFA's.[1, 7, 11, 38, 42–48] Starting from the substituted TFAs, the synthesis of symmetrically substituted trifunctional 3F compounds and monomers of 3F trimethyls, triacids, trinitriles, and triamines has already been reported[11] while the synthesis and uses of pendant 3F triphenols and subsequent derivatives are discussed in section 3.4.5. Also starting from substituted TFAs, the synthesis and uses of unsymmetrically trisubstituted pendant ethynyl 3FBPs are discussed next in section 3.4.2. Similarly, starting from the unsubstituted TFAs, many additional difunctional 3F monomers have also been synthesized by condensations with a variety of aromatics, such as ortho xylene for the 3FDA route[1–7] (fig. 2), toluene for the 3FDCA route,[11, 37] phenols for the 3FBP route,[37, 53–56] aniline for the 3FDAM route[1, 9, 11–12] (fig. 3) and diphenyl ethers for the 3F xanthene diacid route[61–64] (similar to fig. 23). From these 3F basic building blocks, additional 3F compounds/monomers have already been prepared, 3F dicyanates, 3F bis (aminophenols), 3F diacetyls, 3F bis (aminoketones), 3F diacrylates, 3F diacid chlorides, 3F bis (arylchlorides), and 3F tri (perfluorovinyl ethers), for use in advanced 3F polymers (other than in 3F polyimides) as discussed in sections 3.4.2 to 3.4.10 to follow. Also, the 3F xanthene diacid has been successively converted to the diacid chloride, diazide, diisocyanate, and, last, to the diamine (all in reference 62), but none of these have been used in any polymerizations except the two 3F xanthene dianhydrides to prepare polyimides as discussed in section 3.3.6. The overall result is that the wide range of 3F compounds/monomers synthesized clearly reflects very highly on the ease of 3F synthesis capability. Furthermore, use of substituted anilines led to the substituted 3FDAM route[9,49-52,54,60] (section 3.3.2). Thus, the versatility of TFA chemistry clearly is not limited to only the polyimides discussed so far, but instead, 3F technology also provides the synthetic route which apples 3F technology into a wide variety of new 3F monomers. The variety of 3F monomers represents essential building blocks for synthesis of an even wider variety of new advanced 3F polymers, as has started happening in the 1990's. Figure 26 summarizes the synthetic route to the basic 3F building blocks that have been modified to prepare more advanced 3F monomers/polymers, all starting from ordinary TFA's. Of these 3F building blocks, the 3FBP has been used the most often, as follows: unsubstituted (sections 3.4.2 and 3.4.3), pendant substituted (sections 3.4.2 and 3.4.5), derivatized (sections 3.4.4 to 3.4.7), and groups next to the hydroxyl (section 3.4.8). The 3FDAM building block has been used the next most often both as unsubstituted (section 3.4.9) and substituted with groups next to the amine (sections 3.4.7 and 3.4.8). The unsubstituted 3FDCA building block has been used the least often (section 3.4.8). A 3F dihalide has also been synthesized without going through these basic 3F building blocks, and was used only once (section 3.4.10).
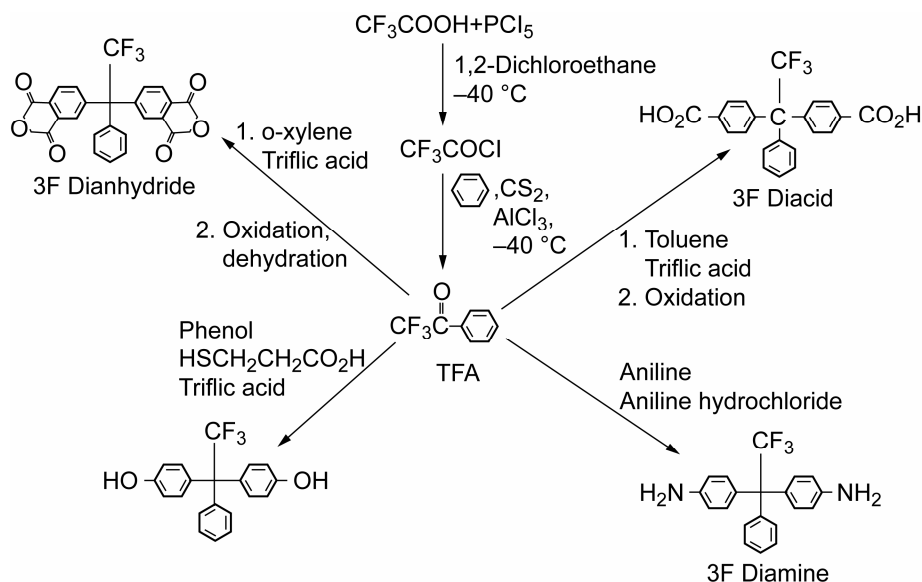
Figure 26.—TFA technology synthesizes 3F monomer building blocks for advanced 3F polymers.

3.4.2 3F Poly (arylene ether)s

Uncrosslinked 3F poly (arylene ether)s have been prepared[55] by the nucleophilic aromatic substitution reaction of 3FBP on the aryl dihalides, e.g., 4,4'-dichlorodiphenylsulfone, 4,4'-difluorobenzophenone (DFB), bis(4-fluorobenzoyl) benzene and bis(4-fluorophenyl) phenylphosphine oxide, by using p-tertiary butyl phenol to control the polymer molecular weight. The resulting poly (arylene ether)s were characterized for molecular weight, intrinsic viscosity, Tg, TOS, refractive index, and polymer solubility/miscibility. The results showed Tgs from 168 to 221 °C, high TOS, a good match of theory and experimental molecular weight, along with many polymer blends being miscible, all as described in reference 55.

Crosslinkable 3F poly (arylene ether)s have also been prepared by the use of ethynyl pendant substituted 3FBP monomers.[44,56] The monomer synthesis was a three step procedure analogous to that used for the ethynyl substituted 3FDAM monomers discussed in section 3.3.3. As before, the procedure was to prepare 4-bromo TFA or 4-iodo TFA, followed by reaction with phenol, instead of with aniline, and last, again the conversion of the bromo group to ethynyl or hexylethynyl substitutents and the conversion of the iodo group to the phenylethynyl substitutent to synthesize ethynyl, hexylethynyl, and phenylethynyl 3FBP monomers (EBP, HBP, and PEBP, respectively); all, coincidentally, in overall yields of 51%. The successful application of an analogous synthetic route further attests to the wide scope of 3F synthetic technology.

As before with the crosslinkable polyimides, ethynyl sites were introduced into 3FBP to crosslink the poly (arylene ether)s in order to control and modify the resulting polymer properties. Thus, crosslinkable 3F poly (arylene ether)s were prepared[44,56] by nucleophilic aromatic substitution of the pendant ethynyl modifed 3FBP with DFB, often producing insoluble polymers as shown in table 11A. Alternatively 10% of EBP, 10% of noncrosslinkable 4-bromo 3F bisphenol (BBP), 10% PEBP and 30% of PEBP were each mixed with 6F bisphenol (6FBP), after which all four bisphenol mixtures and 100% of 6FBP as a control were polymerized with DFB. The resulting five polymers were characterized for inherent viscosity and Tg (table 11B) and TGA-TOS and film mechanical strength (table 11C). The results showed the toughness and solubility of the crosslinkable copolymers could be systematically controlled by varying the amount of ethynyl 3FBPs, which ultimately controlled the final crosslink density, similar to that result shown for the ethynyl crosslinked 3F polyimides in section 3.3.3.

TABLES 11A, B, AND C.—SOLUBILITY, VISCOSITY, Tg, TOS, AND ROOM TEMPERATURE
FILM PROPERTIES OF DFB/ETHYNYL 3F BISPHENOL POLYMERS/COPOLYMERS.

TABLE 11A.—INHERENT VISCOSITY
OF 3F POLY (ARYLENE ETHER)S

Bisphenol monomer	Bisfluoro monomer	$\eta_{inh,}$ dL/g
BBP	DFB	1.15
EBP	DFB	Insoluble
HBP	DFB	Insoluble
PEBP	DFB	0.38

TABLE 11B.—CHARACTERIZATION OF DFB/BPAF-BASED 3F COPOLYMERS

Bisphenol with BPAF	$\eta_{inh,}$ dL/g	DSC Tg, °C	
		Initial	Final[a]
10% BBP	1.4	170	170
10% EBP	0.89	172	185
10% PEBP	0.92	165	179
30% PEBP	0.52	162	184
100% BPAF	0.35	168	168

[a]After heating to 350 °C for 1 hr.

TABLE 11C.—THERMAL STABILITY AND THIN FILM PROPERTIES OF
3F POLY(ARYLENE ETHER) POLYMERS AND COPOLYMERS

Bisphenol with BPAF	5% weight loss by TGA, °C		23 °C tensile properties (150 °C)		
	Air	N_2	Strength, MPa	Modulus, GPa	Elongation, %
10% BBP	484	490	54.5 (28.9)	1.80 (1.58)	60 (76)
10% EBP	461	484	71.0 (33.8)	2.36 (1.79)	6.1 (9.1)
10% PEBP	455	487	68.9 (33.8)	1.96 (1.48)	96 (180)
30% PEBP	452	484	65.5 (31.0)	2.35 (1.60)	4.8 (4.8)
100% BPAF	476	493	65.5 (27.6)	2.24 (1.37)	9.9 (1.3)

3.4.3 3F Polyarylates (3F Aromatic Polyesters)

Polyarylates of 3F aromatic polyesters have been prepared from 3FBP condensed with 6F dicarboxylic acid (6FDCA),[85–86] 4,4'-diphenyldicarboxylic acid (DPDCA),[85–86] terephthalic acid (TA)[87–89] and isophthalic acid (IA).[87–89] Films of the 3FBP/DPDCA polyarylates provided[86] similar TS, E at break and elasticity modulus over a 20 to 250 °C range when compared to four polyarylates made with similar, but nonfluorinated bisphenols (replacing the trifluoromethyl group with hydrogen, methyl, phenyl, and replacing the 3F linkage with a 9,9-fluorene group). The 3F Tgs were all reported[85–89] between 290 and 320 °C in 10 °C intervals except for the IA polyarylate which was 260 °C. The TGA-TOS ($T_{d-incipient}$ and $T_{d-20\% loss}$) in nitrogen were 446 and 484 °C for the TA/3FBP polyarylate compared to 438 and 512 °C for the analogous TA/6FBP polyarylate.[88–89] The TGA weight losses in nitrogen of the 3FBP versus 6FBP/TA polyarylate were initially comparable,[88] with 3F first providing 0.5% less weight loss at 450 °C (thus providing the slightly better 3F $T_{d-incipient}$ in the above sentence). However, the trend dramatically crossed over by 500 °C, with 3F exceeding 6F by 26% weight loss (thus providing the much better 6F $T_{d-20\% loss}$). As temperature increased, 6F accelerated to catch up in weight loss, such that 3F then loses only slightly more weight (4.5%) than 6F at 550 °C, but finally 3% less at 600 °C (thus providing the higher final 3F char yield). Not unexpectedly, the same crossover trend is in total agreement to the trend observed for the 3FDA versus 6FDA/PPDA polyimides shown earlier in figure 4. In fact, the analogous polyarylate TGA figure would look remarkably similar, except shifted about 50 °C lower and the 3F $T_{d-incipient}$ being slightly before the 6F $T_{d-incipient}$ instead of slightly after as in 3F versus 6F polyimide TGAs

shown earlier in figure 4.The disappointing TGA results[85–89] caused the workers to abandon 3F as they were instead actively pursing higher polymeric TOS at that time.

3.4.4 3F Polydimethacrylates for dental composites

The 3FBP has also been incorporated into a set of twelve experimental acrylates[90] by using four different bisphenol connecting linkages, 2,2-propane, phenyl phospine oxide, 6F and 3F, for the bisphenols, each then reacted with three different acrylates, varied by a hydroxyl, hydrogen, and methyl group on the acrylate. This was done to alter the hydrogen bonding, affecting the viscosity for their use as dental composite resins. The state-of-the-art is the Bisphenol A dimethacrylate (Bis-GMA) diluted with triethylene glycol dimethacrylate (TEGDM) in order to obtain an appropriate working viscosity for filling dental cavities. However, more diluents adversely affected the dental composite properties. The initial study[91] only compared the Bis-GMA with methylated 3F Bis-GMA and methylated Bis-GMA. That study found the 3F version provided the correct viscosity range by only using 6.5 to 14% TEGDM diluent compared to 27.5 to 33.5% TEGDM diluent needed for Bis-GMA. The methylated Bis-GMA was too fluid, even without any TEGDM diluent, to be used. This dramatic viscosity lowering effect was accomplished while still providing comparable contact angle, lowest shrinkage during polymerization (6.39 lowered to 5.35%) and lowest water uptake (3.05 lowered to 0.91%), presumably due to the fluorine content of 3F. The later work[90] then incorporated the 6F and phenyl phosphine oxide Bis-GMAs along with the hydrogen substituted acrylates to complete the twelve resin set. In the later expanded data set,[90] the new results showed that now the methylated 6F Bis-GMA was superior to the previously superior methylated 3F Bis-GMA in both lower viscosity (0.8 versus 3.7 pascal seconds), lower shrinkage (4.4 versus 6.3%-undoubtly due to the 6F Bis-GMA did not require any TEGDM dilution), and a comparable low moisture uptake (0.18 versus 0.16%). Thus, 3F technology again came out second best compared to 6F technology as has often happened previously in many other 3F applications. It should also be noted that the lower viscosity for the 6F resin versus 3F is in agreement with the resin remelt viscosity discussed in section 3.1.4, and with the 3F PETI resins discussed in section 3.2.4, but not in agreement with the lower processing viscosity when using reactive diluents as discussed in section 3.2.4.

3.4.5 3F Perfluorocyclobutane Poly (aryl ether)s for Wave Guides

The synthesis capability of 3F technology was also further demonstrated by using a similar route to the 3FBP to synthesize a pendant 3F trisphenol.[92] Para hydroxyl TFA was reacted with phenol to form an additional pendant type 3F compound where all the groups are the same, the 3F trisphenol, in an 85% yield. The 3F trisphenol was then converted to the tri-potassium salt, followed by the nucleophilic displacement reaction on 1,2-dibromotetrafluoroethane to form the tris (2-bromotetrafluoroethoxy) derivative of 3F trisphenol in a 77% yield. A dehalogenation reaction with zinc then formed the tris perfluoro vinyl 3F phenyl ether in a 67% yield. The ease of these syntheses in high yields again reflects highly on the versatility of 3F synthesis technology.

A series of five difunctional perfluoro vinyl ethers, based on various bisphenols containing fluorine, including 6FBP but not 3FBP, was also synthesized.[92] These type of highly fluorinated polymers are desirable because their low amount of carbon hydrogen bonds minimizes optical loss and provides the low CTE and high Tg needed for optical waveguide materials. However, all the difunctional ones provided soluble perfluorocyclobutane containing poly (aryl ethers) of Tg from 91 to 131 °C after the cyclodimerization polymerization. Only the 3F tris perfluoro vinyl ether provided the desirable high Tg (> 400 °C), but was insoluble after both solution and bulk polymerizations. To circumvent the insolubility problem, the 3F tris perfluoro vinyl ether was dimerized as a partial reaction step, thereafter cast into films before completing the thermal polymerization. By this technique, the 3F tris perfluoro vinyl ether provided the lowest CTE (89 ppm/°C versus 104 to 151 ppm/°C) and the highest TGA-TOS in air/nitrogen (449/452 °C versus 382 to 420/399 to 450 °C) while providing a low birefringence (0.0008), and negligible near IR absorbance at 1550 nm compared to the five non 3F perfluorovinyl ethers. Only

the 6F bis perfluoro vinyl ether provided a lower (–0.0005) birefringence, so the author[92] suggested the next work should be to combine the 6F bis perfluoro vinyl ether with 3F tris perfluoro vinyl ether to obtain the correct balance of properties for optical waveguide applications.

3.4.6 3F Polycyanurates

Another derivative of the 3FBP building block is the biscyanate,[93] prepared as one of a series of bisphenols used to prepare dicyanate monomers in unspecified yields, each from their corresponding bisphenols containing phenyl phosphine oxide, sulfone, carbonyl, diphenoxy phenyl sulfone, and 3F linkages. The 3F dicyanate monomer was prepared as one of a series of five dicyanates, each by reacting cyanogen bromide and the corresponding bisphenol at low temperature. After cyclotrimerization of the–OCN group to form the polycyanurates, the 3F polycyanurate provided the highest Tg, widest processing window and second highest TGA-TOS, but only the phenyl phosphine oxide dicyanurate provided any char yield in air TGA (32% at 750 °C compared to 0% for the other four polycyanurates) as reported in reference 93. Thus, 3F again lost out, as later efforts were towards the phenyl phosphine oxide monomer for low flammability resins.

3.4.7 3F Polyquinolines

Another derivative of the 3FBP building block is the diacetyl compound,[94] prepared as one of the two monomer types used for polyquinolines. It was prepared by the nucleophilic substitution reaction of the 3FBP salt on 4-fluoroacetophenone as shown in figure 27. This 3F monomer was then condensed with a derivative of 3FDAM building block, the 3F diamino diphenylacetyl or 3F diamino diacetyl monomer, to produce 3F polyquinolines in examples 3 and 8 of a patent.[94] The patent also reported the work with the corresponding 6F monomers for a total of eight fluorinated linkage monomer combinations, besides using the diamino diacetyls or diphenylacetyls without fluorinated linkages, further expanding the polyquinolines claimed/reported. As long as there was a 3F or 6F in one or the other linkage, the polyquinolines formed had high Tg (200 to 350 °C), low DE, low moisture uptake and good solubility in chloroform, toluene, N,N-dimethylacetamide (DMAc) and NMP. Also claimed in reference 94 are numerous examples of AB acetophenone/ortho aminoketone type monomers, including those with 3F and 6F linkages; however, the examples did not make it clear which AB type monomers had been really synthesized.

3.4.8 3F Polybenzoxazoles

The 3FBP building block was also derivativized into another 3F monomer, the 3F bis aminophenol,[54] for use in synthesizing polybenzoxazoles (PBOs). The original 3F workers[11, 37] prepared the dinitro 3FBP (example 8 of reference 37) in a 74% yield by nitrating the 3FBP in acetic acid/nitric acid to form the 3,3'-dinitro 3FBP. Later workers obtained the same result in a 95% crude yield (75% recrystallized yield), followed by catalytic reduction to the 3,3'-diamino 3F bisphenol (3FAP) monomer in a 99% crude yield (30% reprecipitated yield).[54] The high yields and reaction ease reflect highly upon the capability of 3F synthesis technology; in this case, avoiding nitrating the 3F pendant phenyl, as the phenol ring is much more reactive toward electrophilic substitution than the 3F phenyl ring. This is opposite of what is seen during the nitric acid oxidation of the 3F tetramethyl precursor to 3FDA, in which the 3F pendant phenyl nitrates as easily as the methylated phenyls oxidize during nitric acid oxidation (section 2.1 and references 7 and 8).

Polymerizations in tetrahydrofuran (THF)/NMP with terephthaloyl chloride (TC) produced the poly o-hydroxyl amide (PHA) followed by cyclization to the PBO by using o-dichlorobenzene to azetropically remove the water formed.[54] The complete characterization of the resulting PBO and six additional 3F containing PBOs was reported in a subsequent paper[95] as follows: one 3F monomer, 3FAP, was polymerized with TC, isophthaloyl chloride (IC), 3F diacid chloride (3FAC), 6F diacid chloride (6FAC), and diphenyl ether diacid chloride (ODB) while the other 3F monomer, 3FAC, was prepared[54] by the
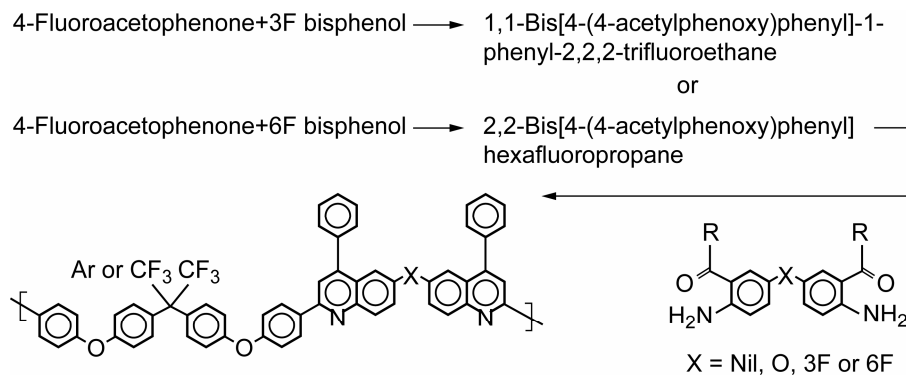
Figure 27.—Representative synthesis pathway to 3F and 6F polyquinolines.

reaction of thionyl chloride and 3FDCA building block and then polymerized with 3FAP, 3,3'-diamino 6F bisphenol (6FAP) and 3,3'-dihydroxybenzidine (DHB).

The paper[95] reported the inherent viscosity of the PHAs and the intrinsic viscosity of the resulting cyclized PBOs along with the Tg and TGA-$T_{d-5\% \ loss}$. This data is shown in table 12. In all five comparisons of 3FAP versus 6FAP monomers, the PBO intrinsic viscosity was always lower for the 3F analogs, and the 3F PBOs were thus slightly more soluble but gave poorer films than their corresponding 6F systems; presumably all these effects being due to the lower 3F molecular weight as evidenced by the lower inherent viscosities. In all the comparisons containing 3FAC versus 6FAC monomers, the PBO intrinsic viscosity was only less for the DHB/3FAC versus 6FAC solution (0.45 versus 0.52); instead being greater when both monomers contained fluorinated linkages, i.e., 3FAP/3FAC versus 6FAC was 0.27 versus 0.26 and 6FAP/3FAC versus 6FAC was 0.48 versus 0.41. Much the same was true for the inherent viscosities of the PHAs. In all cases, the 3F inherent viscosity was less than the 6F inherent viscosity except for DHB/3FAC versus 6FAC (0.73 versus 0.61) and 3FAP/3FAC versus 6FAC (0.29 versus 0.27). The authors[95] also suggest the lower intrinsic PBO viscosities compared to the corresponding higher inherent PHA viscosities are due to degradation during the benzoxazole cyclization, but they also admitted that the evidence is somewhat weak. The apples-to-oranges comparison of the two different viscosities (intrinsic versus inherent) tends to negate the comparison between the two polymer types and the subsequent claims for polymer degradation during the cyclization reaction to benzoxazoles. A later paper[96] republished this data, without the DHB polymers, but with an additional table of solubility data. They did note that the 3F PBOs tended to be more soluble than the 6F PBOs and also included more extensive data on the polymerization method used.

More interestingly, Tg data of the five 3FAP versus 6FAP polymer pairs in table 12 shows that the 3F Tg was always at least equal to and often greater than the 6F analog. However, the three 3FAC versus 6FAC comparisons possible in table 12 show the 3F Tg was roughly equal to or less than the 6F analog, i.e., DHB/3FAC versus 6FAC was 350 versus 345 °C, 3FAP/3FAC versus 6FAC was 330 versus 334 °C while 6FAP/3FAC versus 6FAC was 310 versus 336 °C. The later paper[96] summarized the Tg data saying the 3F versus 6F Tgs were all similar except the 6FAP/3FAC versus 6FAC as noted above. Earlier, the 3F versus 6F polyimide Tg conclusion in section 3.1.1 stated that 3FDA and 6FDA polyimide Tgs were virtually identical while the 3FDAM and 6FDAM polyimide Tgs were consistently higher by 15 to 30 °C for the 3FDAM polyimides. If one views the 3FAC as the same para ring structure as 3FDAM and views cyclized 3FAP as the same ring structure as 3FDA (minus the carbonyls), then the Tg results might show the same trend, i.e., 3FAP/3FAC corresponds to 3FDA/3FDAM, for when a thermal-induced segmental polymer chain rotation is allowed at the 3F or 6F linkage, to define the Tg. Instead the trend seems reversed; for polyimides with the 3FDA gave the same polyimide Tg as 6FDAwhile 3FAP gave a higher Tg than 6FAP. Conversely, 3FDAM gave higher polyimide Tg than 6FDAM, while 3FAC gave only equal or lower Tg than 6FAC. Thus, any quest for higher Tg (3F versus 6F linkages) needs to be examined in each polymer type rather than predicting results by analogy to similar polymer ring

structures. Of much less interest, the TGA-$T_{d-5\%loss}$ reported[95] ranged from 509 to 547 °C without a consistent trend of which would be greater for each 3F/6F PBO pair reported in table 12.

TABLE 12.—SOLUTION AND THERMAL PROPERTIES OF 3F AND 6F CONTAINING POLYBENZOXAZOLES

Z = 6F, 3F, Nil
Ar = DPE, DP3F, DP6F, m–ϕ, p–ϕ
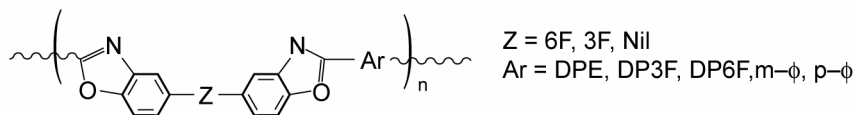
Amino phenol monomer – Acid chloride monomer

Polybenzoxazoles	η_{inh}[a] dl/g	$[\eta]$[b] dl/g	Tg °C	5% Weight Loss °C
6FAP-ODB	0.92	1.08*	280	534
3FAP-ODB	0.48	0.29	299	547
6FAP-3FAC	0.44	0.48	310	529
3FAP-3FAC	0.29	0.27	330	514
6FAP-IC	0.62	0.54*	296	512
3FAP-IC	0.31	0.26	301	524
6FAP-TC	0.65	0.45*	361	531
3FAP-TC	0.37	0.20*	369	536
6FAP-6FAC	0.56	0.41*	336	531
3FAP-6FAC	0.27	0.26	334	520
DHB-6FAC	0.61	0.52	345	534
DHB-3FAC	0.73	0.45	350	509

[a]Inherent viscosity of PHA measured in NMP
[b]Intrinsic viscosity of PBO measured in NMP (unless starred)
*Measured in *m*-cresol

Similar to above, the 3FBP building block was also used to synthesize three other 3F PHAs and PBOs. However, in this report,[97] the 3FBP was expanded to a longer 3F diacid chloride (while above it was nitrated and reduced to the 3F bis aminophenol, 3FAP). The synthesis was done[98] by the nucleophilic displacement of 3FBP on p-fluorobenzonitrile in 72% yield, followed by alkaline hydrolysis to the 3F diacid analog of 3FBDAF, 1,1-bis[4-(4-carboxyphenoxy)phenyl]-1-phenyl-2,2,2-trifluoroethane (3FBDCF), in 98% yield. The diacid was then reported[97] to convert to the 3F diacid chloride in almost quantitative yield by reaction thionyl chloride. As mentioned before, the widening variety of 3F monomers reflects very highly on the versatility and ease of 3F synthetic technology.

A series of three, 3F PHAs and their cyclized PBOs were then prepared using 3FBDCF polymerized with 6FAP, DHB, and 3,3'-diamino-4,4'-dihydroxy-biphenyl (p-DHB). The inherent viscosity (0.5 g/dl in DMAc) of the PHAs was 0.39, 0.62, and 0.98, respectively, after which all viscosities (0.5 g/dl in concentrated sulfuric acid (con. H_2SO_4)) decreased after cyclization to PBOs to 0.29, 0.54, and 0.66, respectively. The three, 3F PHAs were all soluble in NMP, DMAc, N,N-dimethyl formamide (DMF), dimethylsulfoxide (DMSO), while the 6FAP PHA was also soluble in THF and m-cresol, probably from its low molecular weight as indicated by the lowest PHA viscosity. After cyclization to PBOs, the three 3F PBOs were only soluble in con. H_2SO_4, except the 6FAP was also soluble in nonacid solvents, probably because both monomers contain fluorinated connecting linkages. The film properties of DHB and p-DHB PHAs were TS 88 and 82 MPa, E both 18% and TM 2.3 and 2.1 GPa, respectively. After thermal cyclization to PBOs, the film mechanical properties changed to TS 81 and 99 MPa, E 7 and 9%, and TM both 2.2 GPa, respectively. The 6FAP PHA and PBO did not cast suitable films for mechanical testing. X-ray analysis of all six 3F polymers showed they were amorphous. The 6FAP, DHB, and p-DHB/3FBDCF PHAs films were characterized by DSC for Tg (129, 130, and 137 °C, respectively), $T_{endotherm, onset}$ (234, 245, and 248 °C, respectively) and $T_{endotherm, max}$ (296, 280, and 299 °C, respectively). The 6FAP, DHB, and p-DHB/3FBDCF PBOs films were characterized by DSC for Tg (222, 236, and 231 °C, respectively), by TMA for $T_{softening}$ (Ts = 211, 245, and 240 °C, respectively), and by TGA for $T_{d-10\%}$

$_{loss}$ (air = 542, 549, and 539 °C; nitrogen = 556, 562, and 561 °C, respectively) and char yield (nitrogen = 63, 68, and 67%, respectively).

In the same paper,[97] the analogous PHA and PBO polymers were prepared using the methyl analog of 3FBDCF monomer. The characterization of the methyl PHA versus 3FBDCF PHA exhibited similar viscosity, similar film mechanical properties (except lower TS and E for the 6FAP/methyl analog), higher Tgs, and similar $T_{endotherm\ onset\ and\ maximum}$. The methyl PBOs compared to 3FBDCF PBOs exhibited much lower viscosity, similar film mechanical properties (TS, E, and TM), similar Tg, similar T_s and similar $T_{d-10\%}$ in air and nitrogen and similar char yield. The complete comparative characterization data for the 3F and methyl analog polymers is listed in tables 1 to 3 of reference 97.

3.4.9 3F Polyamides

The 3FDAM building block has also been polymerized with TC to prepare polyamides, in this case called polyterephthalamides. The paper[99] reported the polymerization of 3FDAM and 6FDAM with TC in NMP, then comparing the 3F/6F results of intrinsic viscosity (0.40 versus 0.41), Tg (332 versus 323 °C), ITA at 400 °C (1.7 versus 1.8%/hr) and TGA-$T_{d-5\%\ loss}$ (both 460 °C). The results were virtually identical, except that the 3F Tg was 9 °C higher, which agrees with the polyimide Tg results that 3FDAM provides higher Tg than 6FDAM (section 3.1.1). These aramids, along with the BDAF/TC and 9,9-dianiline fluorene/TC polyamides, were reported to have high thermal stability and could be redissolved in polar aprotic solvents. They also all formed fingernail creaseable films. Thus, as has been seen before in many polymer types, 3F appears not to provide any clearcut advantage versus the existing 6F technology, other than the lower cost and the one step 3FDAM monomer synthesis route discussed (originally reported[11] and discussed in section 2.1). Not even the advantageous easier polymerizability[1, 12] (section 2.1) of 3FDAM versus 6FDAM due to the higher reactivity[14–15] was observed or mentioned in reference 99.

Another paper recently reported[98] a more extensive set of 3F modified polyamides using both the 3F analog of BDAF (prepared as discussed in section 3.3.7 and reference 53) and the 3F diacid analog of BDAF, 3FBDCF (prepared as discussed in section 3.4.8 and reference 98). Using the diamine, 3FBDAF , nine polyamides were prepared by the phosphorylation technique with TA, IA, DPDCA, 6FDCA, 4,4'-oxydibenzoic acid (OBA), 4,4'-sulfonyldibenzoic acid (SBA), 5-tert-butylisophthalic acid (t-BIA), 2,6-naphthalenedicarboxylic acid (26NA) and 1,4-naphthalenedicarboxylic acid (14NA). Using the diacid, 3FBDCF, eight more polyamides were also prepared by the phosphorylation technique with PPDA, MPDA, ODA, benzidine (BZ), 1,4-bis(4-aminophenoxy)benzene (p-BAB), 1,3-bis(4-aminophenoxy)benzene (m-BAB), 4,4'-bis(4-aminophenoxy)biphenyl (BABB), and bis [4-(4-aminophenoxy)phenyl]ether (BAPE). All were shown to be amorphorus by x-ray analysis. The seventeen polyamides were extensively characterized for inherent viscosity (0.51 to 1.54 dl./g), M_w (36,200 to 80,000), M_n (17,200 to 64,300), molecular weight peak maximums (20,400 to 135,000), solubility (NMP, DMAc, DMF, DMSO, m-cresol, and THF; most were soluble in all solvents), yield strength (83 to 97 MPa), TS (76 to 94 MPa), E (6 to 69%), M (1.70 to 2.22 GPa), Tg (eight 3FBDCF = 185 to 266 °C, and nine 3FBDAF = 220 to 260 °C), T_s (eight 3FBDCF = 190 to 268 °C and nine 3FBDAF = 222 to 259 °C), $T_{d-10\%}$ (air = 502 to 548 °C, nitrogen = 509 to 563 °C), and char yield (57 to 67%). The complete characterization data is in tables 1 to 3 in reference 98.

In addition to the 3F polyamides, reference 98 also compared the polyamide Tgs and stability via TGA of the methyl analog of 3FBDAF and 3FBDCF with their respective trifluoromethyl analogs (discussed above). The methyl monomers were synthesized, polymerized and fully characterized in reference 100. The comparison of methyl to trifluoromethyl polyamide Tg and T_d data is in table 3 of reference 98. The results showed that the methyl analog polyamides Tg was usually lower by as much as 43 °C and T_d in air was always lower by as much as 65 °C and the T_d in nitrogen was mostly lower by as much as 65 °C.

3.4.10 3F Polyphenylenes

At the American Chemical Society Polycondensation '98 meeting September 27–30, 1998, in Annapolis, Maryland, a talk was presented that reported the polymerization of aromatic dihalides to form 6F based polyphenylenes by the use of nickel catalyzed couplings of the aromatic dihalides. Data was also presented about the extensive characterization of the linear 6F polyphenylenes, however during the presentation a slide showed that the same chemistry had also been done with the analogous 3F dihalide monomer, with the final paper to be published later. However, when the paper[101] was published, it did not also present the limited analogous 3F polyphenylene data, so this review can only say that 3F polyphenylenes have been studied similar to the 6F polyphenylenes in reference 101. It is not known if there has been any work planned or on-going towards preparing a 3F aromatic trihalide for use as a branching point in the linear 3F or 6F polyphenylenes. However, this is an obvious feasible application of 3F as a synthesis technology, as discussed in this review, by using the 3F pendant phenyl to introduce the third halide for use as the branching site. From all the discussion within this review, it should be an easy, high yield, one step reaction for 3 or 4 chloro trifluoroacetophenone to react with chlorobenzene to prepare the 3F triaryl chloride in one high yield step for use in small amounts to branch 3F or 6F polyphenylenes by polymerization techniques in reference 101. A number of trifunctional 3F compounds have been previously prepared as discussed in section 3.3, but the trihalide has not been previously prepared. The pendant phenyl has already been demonstrated in section 3.3.3 as a site to introduce ethynyl groups for crosslinking polyimides in order to control and modify subsequent polymer properties. Thus, this could easily be another demonstration of the capability of superior 3F synthesis technology and the use of a tris monomer to control and modify subsequent polymer properties.

3.4.11 3F Polybenzimidazoles and 3F Pyrones

Although polybenzimidazoles (PBI) and pyrones seem to be obvious uses for the 3F building blocks, 3F DCA, and 3FDA, reports of their reaction with any number of aromatic tetraamines to produce PBIs and pyrones was not found in the literature. If they do exist somewhere, our apologies for our failure to locate them in order to incorporate them into this review.

4. Concluding Remarks

In spite of 3F polyimides clearly being thermo-oxidatively inferior as replacements for 6F polyimides for jet engine applications, all the activity generated after our initial 3F polyimide publication[1] could easily have lead to development of 3F technology as the next generation of low cost, intermediate use temperature fluorinated resins. This includes a wide variety of specialty 3F polymer applications for aerospace and microelectronics because of the lower cost than commercial 6F technology and their expanded synthetic versatility over 6F resins. Thus, it appears that everything 6F does for polymers, except improved TOS and lower dielectric, 3F technology can also achieve. Unfortunately, other than the ability to functionalize the pendant 3F phenyl group to control or modify polymer properties, a clear technical advantage of 3F versus 6F polymers remains elusive, leaving 3F as the "poor mans" 6F polymer technology due to potential lower 3F starting material and synthesis costs. Today, 3F technology still awaits the identification and the subsequent development of additional polymer applications that can not be done using existing 6F polymer technology, instead of being just another "me too" technology. Hopefully, this article will cause that progress to happen. As a result of work to date, nine U.S. patents[2–7, 9, 37, 43] have been issued to the U.S. Government with one licensed[9] to industry. Also, technical interactions with associates have independently resulted in the issue of nine US patents[8, 10, 21, 33–34, 51, 57, 70, 94] to industry. However, without specialized 3F applications being identified, the current state of 3F technology will not be likely to compete or displace the 6F technology that is firmly in place in the marketplace. The market being so small, yet mature, no room seems to exist for the competing 3F polymers technologies. The lower cost and superior expanded synthetic capability of 3F technology has

been clearly demonstrated. Further use of 3F technology clearly depends on creative identification of new opportunities where 3F technology can succeed.

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13. SUPPLEMENTARY NOTES

14. ABSTRACT
A new, lower cost fluorinated dianhydride based on the phenyltrifluoroethylidene (3F) connecting linkage was invented by the principal author in the early 1980's. New 3F condensation and addition cured polyimides were synthesized with the newly discovered 3F dianhydride and the previously known 3F diamine. As controls, polyimides based on the somewhat analogous higher cost hexafluoroisopropylidene (6F) linkage were also prepared. The short term thermal oxidative stability (TOS), determined by thermal gravimetric analysis (TGA), and the glass transition temperatures (Tg) of 3F dianhydride polyimides were found to be similar to 6F dianhydride polyimides, but the Tg was slightly higher for 3F diamine polyimides than 6F diamine polyimides. Unfortunately, in real time testing, long term TOS of 3F polymers was clearly inferior to 6F polymers. This was due to a 3 to 5 fold greater rate of loss of trifluoromethyl group from 3F versus 6F linkages. However, at shorter times or lower temperatures, 3F TOS was almost comparable to 6F TOS. The wide scope of the 3F technology was also demonstrated to have distinct unique advantages over 6F technology through the use of the 3F pendant phenyl ring as a synthetic site to introduce other functional groups. These groups have been used for the control or modification of polymer properties; an advantage lacking within 6F technology. The synthetic ease by which 3F can be introduced into various types of monomers has lead to the explosion of advanced 3F polyimides and other high performance advanced 3F polymers in the prior decade of 3F polymer literature as cited herein; covering polyimides, substituted polyimides, at least ten types of nonpolyimide 3F polymer modifications, and also the government's nine 3F U.S. patents and corporations' nine 3F U.S. patents.

15. SUBJECT TERMS
Glass transition temperatures; Fluorinated polymides; Polymer/composite thermo-oxidative stability; 3F ploymers/composites; Microelectronic and gas separator polyimides; High temperature polymers

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