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Synthesis and Properties of Highly Fluorinated Polyimides

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ABSTRACT: A series of polyimides was synthesized to facilitate the study of several structure/property relationships, including relative permittivity, moisture absorption, free volume, and viscoelastic transitions. This series was based on hexafluoroisopropylidene bis(phthalic anhydride) and various diamines, with the intention of having a number of fluorine/hydrogen and symmetric/asymmetric analog sets. Since several of the fluorinated diamines were exceptionally unreactive, a multistep polycondensation polymerization technique was developed to obtain materials of sufficient molecular weight for property evaluation. Effects of fluorine incorporation on the aforementioned properties are reported.

Introduction

Polyimides are a class of polymers that are highly thermally stable and that have high glass transition temperatures, wide chemical resistance, and relatively low dielectric constants. They are distinguished from other high-performance polymers by the solubility of the poly(amic acid) precursor form, which can be cast into uniform films and quantitatively converted to the polyimide. For these reasons, polyimides have found wide use in microelectronic and aerospace engineering.

The incorporation of fluorine into polyimide structures has been intensively explored in the past decade with the hope of fine-tuning several properties of particular interest. Fluorine incorporation has been found to generally lower the dielectric constant[1-9] and moisture absorption,[10-12] to bring about desirable changes to optical properties,[13-16] and also to increase the thermal stability in some cases.[2,17] While there have been occasional forays into more complex fluorinated structures[18-21] with valuable results, most work has concentrated on the incorporation of the hexafluoroisopropylidene moiety (6F) into dianhydride and diamine components.[22] This concentration of effort was presumably due to the fact that significant property enhancement was realized with the 6F group and because other fluorinated monomers have been hard to come by. Few are commercially available, and they are relatively difficult and expensive to synthesize. Many synthetic conversions leading to the selective placement of fluorine atoms and CF_3 groups are not well characterized or require lengthy multistep procedures with discouraging yields.

The steric and electronic characteristics of the fluorinated groups can reduce the reactivity of the nucleophilic component of a polycondensation reaction to the point where polymerization is suppressed or effectively precluded. Polyimides are usually synthesized via a typical AA–BB type polycondensation, with component AA consisting of a dianhydride and component BB consisting of a diamine. A precursor poly(amic acid) is initially formed via nucleophilic attack by the diamine at a carbonyl carbon of the dianhydride. The rate of this reaction is largely dependent on the electron-donating potential of the amine and on the electron affinity of the anhydride. Although the ways in which fluorine atoms and trifluoromethyl groups affect the basicity of an amine and the electron affinity of an anhydride carbonyl is complex,[23] it is fair to generalize that the high electronegativity of fluorine acts to reduce the basicity of amines and to increase the electron affinity of anhydrides. Thus polyimides made with fluorinated diamines tend to have to be coaxed to high molecular weight, while polyimides made with fluorinated dianhydrides are generally quite reactive. There are, however, few fluorinated dianhydrides because of the much greater difficulties involved in their synthesis relative to diamines, where intermediate nitro groups can be taken advantage of to activate aromatic coupling reactions.

The primary aim of the work reported here was to synthesize an appropriate series of polymers to facilitate the study of structure/property relationships of fluorine-containing polyimides and to report some tentative generalizations derived from the results. Some new approaches to polycondensation of systems with limited reactivity were developed to obtain this group of new polymers—namely, a multistep condensation where the first step is a standard solution polycondensation while the second and any subsequent steps are solid-state chain extension reactions. Some exploration of the chain extension process will be discussed, as well as some structure/property findings. The polymer series studied was essentially limited to those obtained from the 6F dianhydride because it proved to be the only dianhydride with which many of the fluorinated diamines would form polymer films suitable for physical characterization.

Our main goal was to learn about the effect of fluorine substitution on the dielectric properties. This involves simultaneous changes to water absorption, free volume, and polarization. This paper will report general dielectric trends and will consider the effect on dielectric constant due to changes in hydrophobicity that results from fluorine substitution. The effect of fluorine substitution on the dielectric constant due to change in free volume and polarizability will be reported separately.[24,25] Several other properties will be briefly considered here as well.

Experimental Section

The following is a general description of the synthesis of the polyimides made for this study. Variations applied to each material are discussed individually.

Synthetic Procedure. Diamines were vacuum sublimed, usually only after solvent recrystallization. Dianhydrides were bought as electronics grade or better and usually used as received (although sublimed 6FDA produced polymer solutions that were less colored).

The polyimide synthesis begins with the drying of the already purified monomers. Diamines were kept dry by storing them in a vacuum desiccator with $CaSO_4$ (Drierite) and were used directly. Dianhydrides were also stored under desiccator conditions but were further dried by heating under vacuum to 100 °C overnight before use.

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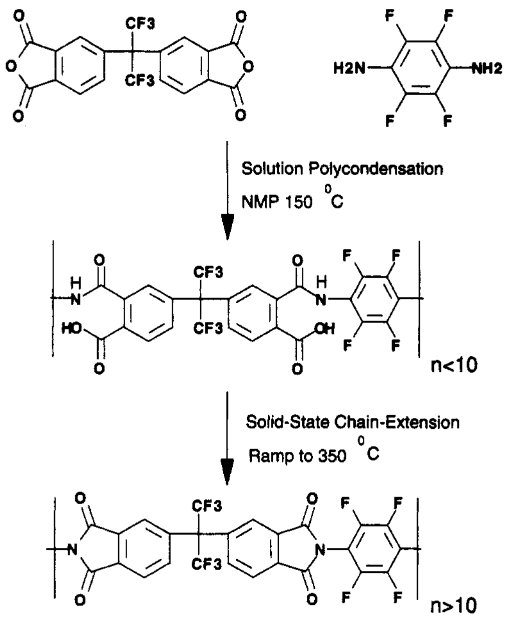


Figure 1. Two-step synthetic procedure for use with deactivated diamines. Second step accomplishes both imidization and chain extension.

The solvent generally used was *N*-methylpyrrolidinone (NMP), which was bought as Sure-Seal anhydrous grade and vacuum distilled from P_2O_5 before use. The first and last fractions were discarded. Substantial variation in the quality of the as-bought solvent was found. When used without distillation, this sometimes resulted in polymer solutions that were opaque and dark brown instead of transparent and either colorless or faint yellow.

The polymers utilizing fluorinated diamines were generally obtained via a two-step process, illustrated in Figure 1, using 6FDA-TFPDA as an example. In the first step, equimolar quantities of dianhydride and diamine were added to NMP in a round-bottom flask and brought to 15% by weight concentration with additional NMP. Usually the dianhydride was added first. All additions were performed under dry argon, which was then kept flowing over the solution during the course of the reaction. During reactions requiring the use of higher temperatures, argon was bubbled directly into the solution.

In most cases involving diamines with F or CF_3 substitution ortho to the amino groups, the resulting solution had a very low viscosity, indicating that only low molecular weight oligomers had formed. This ortho deactivation has been noted previously.[26]

To make durable and uniform polymer films suitable for dielectric constant measurements, 3–4 mL of these low-viscosity polymer solutions was added dropwise by syringe through a Millipore disposable filter (5-μm pore size) onto a 2.25 in. diameter × $^1/_8$ in. quartz disk which was resting on a level glass table in a vacuum oven. After applying 20–25 in. Hg vacuum for 1 h (or as long as required for complete removal of bubbles), a slight nitrogen purge was introduced to assist the drying, and the temperature was set to 60 °C. After a drying period of between 8 h and overnight, the oven was cooled to room temperature and the quartz disk, with the sometimes extremely fragile and low molecular weight poly(amic acid) film, was carefully removed to the high-temperature tube furnace. The sample was heated under nitrogen at a rate of 1 °C/min to a final temperature of 350 °C, held there for 1 h, and then slowly cooled. The rate of 1 °C/min was required to avoid bubble formation during cure.

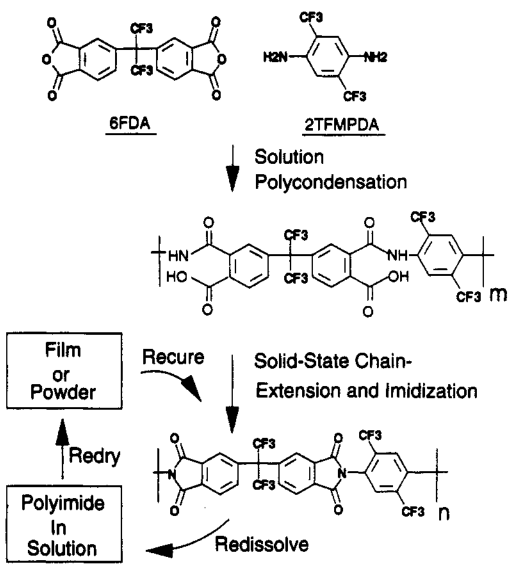


Figure 2. Cyclic chain extension synthetic procedure for use with extremely deactivated diamines. Degree of polymerization increases with number of cycles.

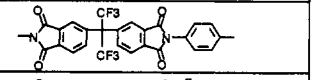
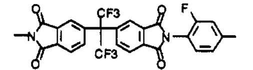
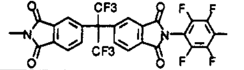
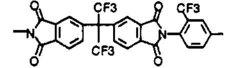
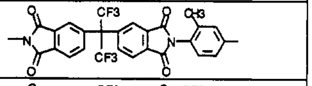
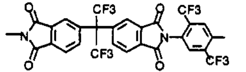
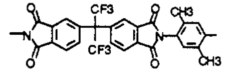
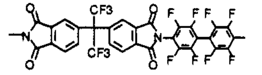
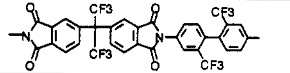
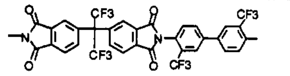
Polymer	Structure
6FDA-PDA	
6FDA-FPDA	
6FDA-TFPDA	
6FDA-TFMPDA	
6FDA-DAT	
6FDA-2TFMPDA	
6FDA-2DAT	
6FDA-OFB	
6FDA-22'PFMB	
6FDA-33'PFMB	

Figure 3. Chemical repeat structures.

The cured polymer film was removed from the quartz disk by immersion and gentle agitation in dilute (5%) aqueous HF (in a fume hood) and was thoroughly rinsed in distilled water and dried.

Two amines of particularly low nucleophilicity were reacted with 6FDA using a cyclic chain extension approach, illustrated in Figure 2, which will be described when discussing the specific synthesis of 6FDA-2TFMPDA. Figure 3 shows the chemical repeat unit structures of all the polyimides prepared from 6FDA.

Specific Polymers. This section discusses monomer preparation and those details of polymerization that differ from the general procedure described above.

6FDA-PDA. 1,4 Diaminobenzene was purchased from Aldrich Chemical as a zone-refined material and was used as received. Mp = 145 °C.

Polymerization of PDA with 6FDA was carried out by adding equimolar amounts of the two monomers to NMP and stirring overnight at room temperature under argon. The resulting solution was colorless and had the viscosity of a light pancake syrup, indicating a moderate but not high molecular weight.

6FDA-FPDA. 1,4-Diamino-2-fluorobenzene (FPDA) was synthesized by S. Pendharkar and A. C. Misra of Polytechnic University according to the procedure of Ishikawa.[27] Mp = 87–89 °C.

Polymerization of FPDA with 6FDA was carried out by mixing equimolar amounts of the two monomers in NMP and stirring at room temperature overnight. A somewhat viscous, colorless solution resulted.

6FDA-DAT. 2,5-Diaminotoluene (DAT) was purchased from Aldrich Chemical as a gray technical grade powder in the form of a sulfate salt and was converted to the amine by slow addition of KOH to an aqueous suspension under airless conditions. It was found that the free amine in solution was highly susceptible to oxidation. The preparation of clean diamine required the use of vacuum-degassed and nitrogen-purged solvents (water and ethyl ether) and reagents (KOH in water) and a continuous purging with nitrogen during every step of the workup.

The polymerization of DAT with 6FDA was straightforward, since the reactivity of the amine toward nucleophilic opening of the anhydride was good. Mixing equimolar amounts of the monomers in NMP at room temperature under a blanket of argon produced a viscous, and colorless solution overnight.

6FDA-TFMPDA. 1,4-Diamino-2-(trifluoromethyl)benzene was obtained from Mitsui Chemical (Japan). It was supplied as a dark red technical grade product and was easily purified to a white powder by vacuum sublimation at 50 °C. Mp = 54–55 °C.

Polymerization of this material with 6FDA was carried out under a variety of time and temperature conditions. After all condensation reactions a nonviscous pale yellow solution was obtained. It was found to our surprise that the best final films, following chain extension, were obtained using room temperature condensed solutions.

6FDA-2DAT. 2,5-Diamino-4-methyltoluene (2DAT) was purchased as a dark yellow technical grade material. It was purified by two successive airless recrystallizations followed by two successive vacuum sublimations to give an off-white product. Mp = 149 °C.

Polymerization of 2DAT with 6FDA was straightforward as the reactivity of the amine was good. Equimolar amounts of the monomers were added to NMP and allowed to stir overnight at room temperature in an argon atmosphere. A viscous, light yellow solution was formed.

6FDA-2TFMPDA. The monomer 1,4-diamino-2,5-bis(trifluoromethyl)benzene (2TFMPDA) was purified by recrystallization followed by vacuum sublimation. Mp = 129 °C.

Polymerization of 2TFMPDA with 6FDA was carried out under a variety of time and temperature conditions (from room temperature to 200 °C). A nonviscous, pale yellow solution was obtained in all cases. The room temperature solution was found to be superior to the higher temperature condensed materials for film formation. However, none of these conditions were able to produce films durable enough for handling using the standard curing and chain extension procedure. These films were badly cracked and extremely fragile. A modified scheme, which we refer to as the "cyclic process", was developed that ultimately succeeded in making mechanically durable films from this amine and others of particularly low reactivity.

This procedure, illustrated in Figure 2, was necessary to obtain continuous and durable films with 6FDA-2TFMPDA. To try to coax the low molecular weight polyimides produced from the sequential solution and solid-state steps into film formation, we tried redissolving the already-cured material (these materials are soluble as the imide), redrying, and recuring. This resulted in a cracked and discontinuous film as well, but the cracking was not quite as severe. Upon a third such redissolving and redrying, the dried film was smooth and continuous, and upon recuring, this dried film remained intact and produced a uniform and strong final film. It seemed that on the first cure the poly(amic acid) underwent imidization and that some chain extension also occurred. Upon the second curing, additional chain extension occurred but to an insufficient extent to give a strong final product. With the third cure the molecular weight apparently reached a critical value for good mechanical film properties. Some point must be reached in this total cyclic process where the material's tensile strength exceeds the stress from shrinkage that occurs during both additional reaction of unreacted end groups and from solvent loss. This cyclic process and the normal single-step chain extension will be discussed in greater detail later.

6FDA-TFPDA. 1,4-Diaminotetrafluorobenzene (TFPDA) was purchased from Columbia Chemical (Camden, SC) as a technical grade product and was recrystallized 2–3 times from methylene chloride until off-white, 0.5-in.-long, needlelike crystals were obtained. After overnight vacuum drying, these needles were sublimed once or twice until stark white sublimate was obtained. Mp = 147 °C.

Polymerization of TFPDA was carried out with 6FDA by adding equimolar amounts of the two monomers to NMP under argon. Various temperatures were used ranging from room temperature to 200 °C but it was found that strong final polymer films resulted after a subsequent solid-state chain extension step only if solution polymerization was carried out at temperatures in excess of 130 °C for 5 h.

The resulting poly(amic acid) oligomer solutions were of extremely low viscosity (indistinct from NMP alone by eye).

6FDA-22′PFMB. 2,2′-Bis(trifluoromethyl)benzidine (22PFMB) was synthesized by Marshalton Research Labs (Winston-Salem, NC) using the procedure described by Gaudiana[28] and was used as received. Mp = 180–181 °C. Polymerization at room temperature produced viscous, colorless solutions overnight.

6FDA-33′PFMB. 3,3′-Bis(trifluoromethyl)benzidine (33PFMB) was synthesized by Marshalton Research Labs using a procedure similar to that for the 22PFMB isomer. 3-Bromo-6-nitrobenzotrifluoride was coupled through the bromine with copper catalyst under Ullman conditions. It was used as received. Mp = 116.5–117.5 °C.

Polymerization with 6FDA was carried out by mixing equimolar amounts of the two monomers in NMP and stirring overnight at room temperature. This resulted in a solution with negligible viscosity, again presumably due to the severe steric and electronic deactivation caused by the ortho trifluoromethyl group. Durable polymer films were successfully produced using the cyclic solid-state chain extension approach.

6FDA-OFB. Octafluorobenzidine (OFB) was purchased from Aldrich Chemical and was recrystallized twice from methylene chloride before vacuum sublimation at 50 °C to obtain a microcrystalline white powder. Mp = 177 °C.

Polymerization of OFB with 6FDA was carried out by mixing equimolar amounts of the monomers in NMP under argon and heating it to a variety of temperatures (from room temperature to 150 °C) for various lengths of time. It was found that durable, self-supporting films were obtained after the solid-state chain extension reaction only if the solution polycondensation had been carried out at temperatures in excess of 130 °C.

Other TFPDA-Based Polymers. The syntheses of three polymers with the TFPDA diamine using the dianhydrides PMDA, BPDA, and BTDA were attempted. In all cases only granular products were obtained and none were film forming. Also, since none were soluble as the imide, the molecular weight growth achievable from the cyclic solid-state chain extension processes (as used, for example, with 6FDA-2TFMPDA) was not possible.

BPDA-TFPDA. 3,3′,4,4′-Biphenyltetracarboxylic dianhydride (BPDA) was obtained from Chriskev Co., Inc. (Leawood, KS), in electronics grade and was used as received. BPDA and TFPDA were reacted in solution under a variety of conditions ranging from 200 °C for 5 h to 75 °C for 85 h. Under no circumstances did any of these materials form films. They produced granular powders only, and their number-average molecular weights by GPC were never higher than around 900. All attempts to make it to sufficient molecular weight for film formation failed.

BTDA-TFPDA. 3,3′,4,4′-Benzophenonetetracarboxylic dianhydride (BTDA) was purchased from Aldrich Chemical in high purity and was used as received. It was reacted with TFPDA under several time and temperature conditions ranging from 150 °C for 5 h to room temperature for 8 days; however, films could not be produced from these solutions, and only granular powders resulted.

PMDA-TFPDA. Pyromellitic dianhydride (PMDA) was purchased in zone-refined form from Aldrich Chemical and was used as received. PMDA was reacted with TFPDA at 150 °C for 5 h and at 200 °C for 5 h. The solution after the 200 °C condensation became turbid and polymer precipitated. The 150 °C product remained clear but produced only powders upon curing. No films were produced.

Molecular Weight Characterization. Gel permeation chromatography was used to characterize the average molecular weight of the poly(amic acid) oligomer after the solution-stage condensation reactions, and to a more limited extent for polyimide materials after high-temperature curing.

A Waters HPLC system was used with a column series consisting of 10000-, 1000-, 500-, and 100-Å Ultrastyragel columns that were continuously heated to 40 °C. A THF mobile phase at 1 mL/min was used which was prepurged with He and kept under a constant 3-psi He pressure head. Nitrogen was used initially, but because of its apparently greater pressure-dependent solubility in THF, it was found to cause retention time drift due to in-line bubble formation.

A series of 14 polystyrene standards (PS) were used to develop a calibration curve of log (molecular weight) versus retention time, and a linear fit was used to assign PS-relative molecular weight values to the unknowns.

Results and Discussion

The results of these molecular weight measurements, after the solution-stage polycondensation only, are shown in Table 1 for all 6FDA-based polyimides. Table 2 shows the number-average molecular weight (M_n) and the M_n for the highest oligomer present. The GPC molecular weight results for 6FDA-2TFMPDA in a cyclic series are shown in Table 3.

Table 1. Number-Average Molecular Weight of Solution Stage by GPC

polymer type and reaction conditions	M_n
6FDA-PDA, room temp, several days	6680
6FDA-PDA, room temp, several days	10484
6FDA-FPDA, room temp, overnight	23246
6FDA-DAT, room temp, overnight	9890
6FDA-TFMPDA, 150 °C, 10 h	2384
6FDA-TFMPDA, 150 °C, 10 h	2219
6FDA-TFMPDA, room temp, many days	2944
6FDA-TFMPDA, 200 °C, 7 h	3714
6FDA-TFMPDA, 100 °C, 5 h	2441
6FDA-TFMPDA, 150 °C, 5 h	1706
6FDA-2DAT, room temp, overnight	5454
6FDA-2TFMPDA, 100 °C, 22 h	1659
6FDA-2TFMPDA, 100 °C, 22 h	1163
6FDA-2TFMPDA, room temp, 4 days	1718
6FDA-2TFMPDA, 60 °C, 30 days	1353
6FDA-2TFMPDA, room temp, 4 days	1656
6FDA-TFPDA, 150 °C, 5 h	910
6FDA-TFPDA, 130 °C, 8 h	1084
6FDA-22′PFMB, room temp, overnight	27378
6FDA-OFB, 125 °C, 5 h	1163

Table 2. Number-Average Molecular Weight of Solution Stage and M_n of Highest Oligomer

polymer	film forming	M_n	M_n(max)
6FDA-TFPDA, 150 °C, 5 h	yes	1381	3957
6FDA-TFPDA, 130 °C, 5 h	yes	940	3586
6FDA-TFPDA, room temp, 5 days	no	1106	1968
6FDA-OFB, 200 °C, 5 h	yes		
6FDA-OFB, 150 °C, 5 h	yes	1480	7102
6FDA-OFB, 50 °C, 5 h	no		
BPDA-TFPDA, 200 °C, 5 h	no	862	2600
BPDA-TFPDA, 140 °C, 5 h	no	883	2468
BPDA-TFPDA, 75 °C, 5 h	no	714	2594
BPDA-TFPDA, 75 °C, 85 h	no	890	2500
BTDA-TFPDA, 150 °C, 5 h	no		
BTDA-TFPDA, room temp, 8 days	no		
PMDA-TFPDA, 150 °C, 5 h	no		

Table 3. Molecular Weight of 6FDA-2TFMPDA after Successive Curing Cycles

T_{max} of cure	M_n
dried at 100 °C (poly(amic acid) precursor)	1216
250 °C	7537
250 °C	9457
300 °C	25353

From the data in Table 2 it can be seen that 6FDA-TFPDA, after solution polymerization at lower temperatures, was unable to produce films after a single high-temperature cure of the type shown in Figure 1, but solutions run at higher temperatures did. While the M_n values of the three solutions are similar, the M_n of the highest oligomer present was twice as high. This implies a lower limit of the initial molecular weight from which a single high-temperature cure could increase the molecular weight to a critical value for mechanical durability.

Chain Extension. In contrast to traditional polyimide synthetic procedures, which are generally quite straightforward, the synthesis of polyimides from many of the fluorine-containing diamines proved challenging because of the severely attenuated basicity of the amine groups adjacent to fluorine atoms or trifluoromethyl groups. The viscosity of solutions after the initial polycondensation was usually indistinguishable (by eye) from the viscosity of the initial mixture, and in these cases, films that were simply cast and cured, under conditions typical for nonfluorinated polyimides, usually produced badly cracked films or granular powders. Two exceptions to this, with fluorine-containing amines, were 6FDA-22′PFMB and 6FDA-FPDA, which both produced initial solutions with significant viscosities and molecular weights and which were film forming. With 22′PFMB this was presumably

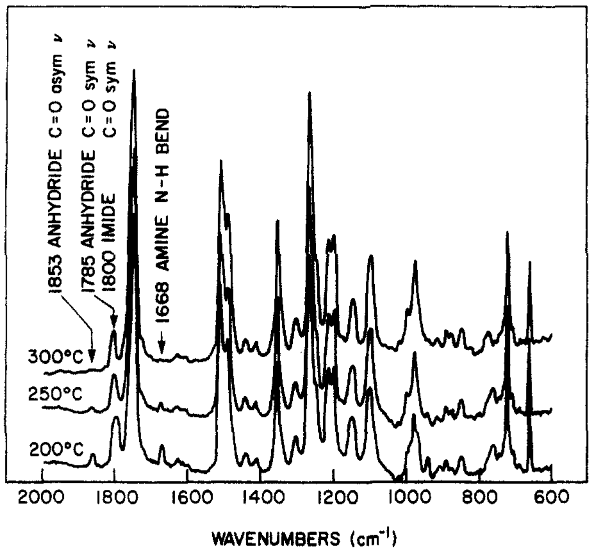


Figure 4. FTIR of 6FDA-OFB after 200, 250, and 300 °C cures, showing gradual decline in end group concentration due to solid-state chain extension.

due to the fact that the meta CF_3 groups are distant from the amino groups, thus exerting no steric influence on reactivity and a smaller electronic effect than if they were ortho. With 6FDA-FPDA the influence of a single fluorine atom is apparently relatively small both sterically and electronically, and so even though fluorine was ortho to the amine, it had only a minimal effect on the reactivity.

We were able to get around these reactivity problems with all the other diamines by taking advantage of the further reaction that takes place between the amine and anhydride during the high-temperature solid-state curing step. This allowed us to acquire materials of adequate and sometimes ample molecular weight for formation of durable films, even with the least reactive species, as can be seen in Table 3. At first glance the single-step procedure we used to take advantage of chain extension in the solid and the traditional synthetic procedure for typical non-fluorine-containing polyimides do not appear to differ greatly, since Figure 1 looks quite standard for polyimide curing. However, the curing conditions were tailored with this chain extension in mind to allow us to maximize the occurrence of polycondensation in the solid, while minimizing film blistering, which would render the films unsuitable for dielectric constant measurement. Other workers have previously observed that melt polymerization can sometimes result in higher molecular weight than the more standard solution polymerization,[29] and we hoped (and found) that molecular weight growth would occur in these polyimides when the solid films were heated to high temperatures. After much trial and error, we found that slow cures which reached temperatures in excess of 350 °C could produce strong films that were smooth and crack free, often in a single step.

The main issues affecting the extent and nature of the chain extension are end group reactivity, chain mobility, and end group mobility. The latter two in turn involve viscoelastic transition behavior and the role of entrapped solvent in plasticizing chain and end group mobility.

Figure 4 shows that the amine and anhydride end groups in 6FDA-OFB which are present after high-temperature solution polycondensation are still present after a 200 °C solid-state cure, are partially consumed by 250 °C, and are fully consumed by 300 °C. As FTIR has a detection limit of around 3–5%, considerable concentrations of end groups may remain, but the film properties are dramatically improved, giving a strong, intact, and uniform film.

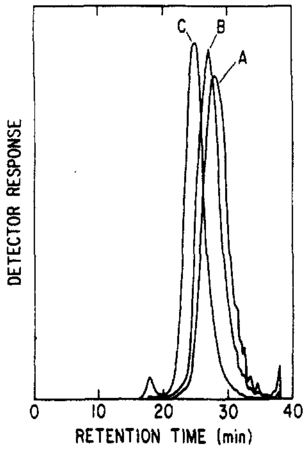


Figure 5. GPCs of 6FDA-2TFMPDA after (A) 250 °C, (B) 2 × 250 °C, and (C) 2 × 250 + 300 °C cure, showing steady increase in molecular weight due to chain extension in the solid state.

Cyclic Variation of Chain Extension. When we attempted to prepare 6FDA-2TFMPDA in the same way that we had successfully prepared the other 6FDA-based materials with fluorinated diamines (in a single, slow high-temperature curing step to afford solid-state extension), we were unsuccessful. Despite the fact that the original oligomer solutions dried into uniform films, the films after the solid-state cure were badly cracked, flaking, and brittle. Many different solution-stage conditions were tried, but all failed in the solid-state cure to produce durable and self-supporting films.

It appeared that the molecular weight was insufficiently increased by this single solid-state cure to give adequate mechanical properties. In addition to the minimal basicity of such a highly fluorinated species, the chains may not have had enough mobility to allow the chain ends to diffuse over a large enough volume to find and react with a sufficient number of other chain end groups to raise the average molecular weight above its critical value required to withstand the stresses of curing. On the assumption that the inadequacy of the first cure was indeed partly due to limited chain extension, we reasoned that if the polymer film fragments could be redissolved and recast, a new set of chain ends would be placed within a reasonable diffusion volume to allow further chain extension to occur on a second high-temperature cure.

On this premise we cured a new sample to only 250 °C (to ensure that it would redissolve), then dissolved the fragments of the 6FDA-2TFMPDA again in NMP, redried it, and recured it to 250 °C. We found that although it was still cracked and flaking, the film quality had improved somewhat. We repeated this cycle a third time, and an intact and durable film resulted. This led us to believe that the chain extension was indeed occurring (even at 100 °C below T_g) and was a critical molecular process in the synthesis of these materials. This is illustrated in Figure 2.

To further explore this process we cured 6FDA-2TFMPDA to 250 °C, redissolved, redried, and recured it to 250 °C, and finally redissolved, redried, and recured it to 300 °C. Samples taken after each stage of these three cycles were then measured by GPC to determine their number-average molecular weights. The results are shown in Table 3 and in Figure 5. It can be clearly seen that the molecular weight after each step increases significantly. This provided us with direct evidence that chain extension was occurring and was responsible for the gradual improvement in the polymer properties.

We cannot distinguish a chain end redistribution explanation from the possibility that the critical factor is

Table 4. Density and Dielectric Properties

polymer	ρ (g/cm^3)	$n^2_{632.8\mathrm{nm}}$	$\epsilon'_{\mathrm{dry,1kHz}}$	$\epsilon'_{\mathrm{wet,1kHz}}$
6FDA-PDA	1.4494 ± 0.0008	2.506	2.81 ± 0.024	3.222 ± 0.0284
6FDA-FPDA	1.4835 ± 0.0056	2.4825	2.85 ± 0.041	3.192 ± 0.0135
6FDA-DAT	1.4316 ± 0.005	2.4888 ± 0.0063	2.75 ± 0.023	3.157
6FDA-TFMPDA	1.4956 ± 0.0096	2.3975 ± 0.0019	2.72 ± 0.005	3.054 ± 0.042
6FDA-2DAT	1.4250	2.42923 ± 0.0102	2.74 ± 0.039	3.212 ± 0.075
6FDA-2TFMPDA	1.5021 ± 0.0019	2.28872 ± 0.0058	2.59 ± 0.03	2.868 ± 0.080
6FDA-TFPDA	1.5305	2.3756 ± 0.0025	2.68 ± 0.046	2.905 ± 0.027
6FDA-OFB	1.5544 ± 0.0004	2.3492 ± 0.012	2.55 ± 0.02	2.729 ± 0.024
6FDA-22′PFMB	1.47895 ± 0.003	2.3823 ± 0.0007	2.715 ± 0.035	2.886 ± 0.0283
6FDA-33′PFMB	1.4627	2.3281	2.568	

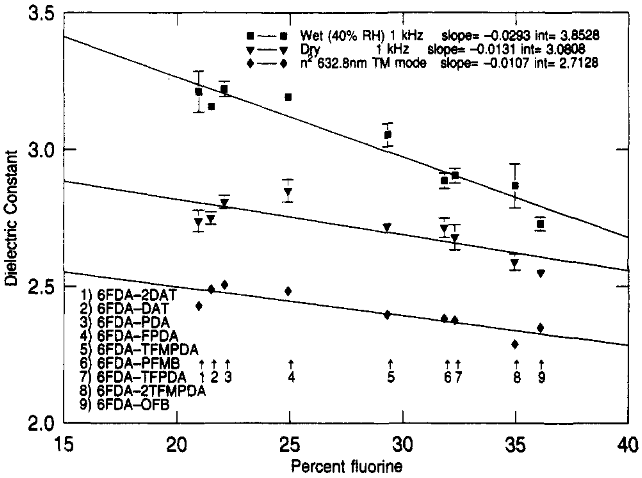


Figure 6. Three data sets are the refractive index squared, the 1-kHz dry dielectric constant, and the 1-kHz wet dielectric constant.

the cyclic reinfusion of solvent into the process, which could plasticize chain end movement. These are separate processes but are similar in that both effectively give a chain end, which has depleted its reactive probability, access to new reactive partners in the polymer matrix.

The general importance of polymer chain mobility in polyimide curing has been recognized for some time with respect to its role in mediating the cyclodehydration process.[30-33] The redissolving of a cured polyimide to facilitate new favorable backbone conformations for cyclodehydration has been found to allow further extents of cure and the reacquisition of the fast initial rate constants observed early in the first cure.[34] While not directly related, these studies show the importance of chain mobility in chemical transformation of the extremely rigid polyimide systems and thus support the plausibilty of chain mobility as a limiting factor in molecular weight extension in the solid state as well.

We acknowledge that without control samples bearing identical thermal histories, but that have not undergone the intermediate redissolving, we cannot conclusively distinguish between the three possible mechanisms: redistribution of chain ends during redissolve–recast steps, renewed plasticization by infusion of additional solvent by a redissolve step, or simply a longer total cure time leading to more chain extension.

It remains clear, however, that significant molecular weight growth is occurring in the solid state and has afforded a means of synthesizing materials previously unattainable for study.

Dielectric Properties. The dielectric constant (ϵ') of each material was measured under three conditions: 1 kHz after equilibration at 40% relative humidity, 1 kHz after exhaustive in-situ drying, and at 632.8 nm. These data are shown in Table 4 and in Figure 6 plotted as a function of percent fluorine. Under each measurement condition, the general trend is for the ϵ' to decrease as a function of increasing fluorine content, though there are exceptions which will be discussed. There are three main ways that fluorine incorporation can affect the dielectric constant: changing the hydrophobicity which eliminates water, changing the free volume, and changing the total polarizability. The first will be discussed, but the second and third will be only briefly be mentioned here.

The n^2 values in Figure 6 are smaller than the 1-kHz values because at optical frequencies only the electronic polarization contributes to ϵ'. While the general trend is decreasing, with a best fit slope of −0.0107, there are exceptions, especially in the first few points. This is due to the fact that while these methylated materials are of low fluorine content, they are partially aliphatic, which leads to lower ϵ'. We can see that the 1-kHz dry data are very similar. The slope of this linear best fit is −0.0131. This trend is also imperfect, as the first four data points show a distinct upward trend. The trend of the first three is again due to the greater aliphatic character of 6FDA-DAT and 6FDA-2DAT compared to that of 6FDA-PDA, but the fourth point for 6FDA-FPDA is significantly higher than 6FDA-PDA, whereas it was smaller at the optical frequencies. This is a fluorinated material and so may at first be expected to be lower than that of 6FDA-PDA because of the lower electronic polarizability of the carbon–fluorine bond relative to the carbon–hydrogen bond. As is more fully considered in another report[25] that focuses on these polarization changes, this is due to the fact that the total polarizability of the 6FDA-FPDA material is indeed higher than that of 6FDA-PDA at this low frequency because of the dipole orientation that occurs as a result of physical oscillation of the entire fluorine-substituted phenyl ring. It deserves note that of the remaining data points those polymers with asymmetrically placed fluorinated groups on the amine phenyl ring generally have a higher ϵ' for a given percent substitution than those with symmetrical substitution.

The dielectric constants taken after equilibration at 40% relative humidity show a dramatically increased slope of the least squares best fit curve, −0.0293, relative to the dry data. This is a clear indication that a difference in the hydrophobicity of the materials as a function of the amount of fluorine in the structure leads to differences in the ambient dielectric constant of the materials. Since the polymers of lower fluorine content absorb more water, and the dielectric constant of water is very high ($\epsilon'_{\mathrm{free}} \simeq 80$), a trend of decreasing dielectric constant with increased fluorine content exists that is due solely to the trend in hydrophobicity, and this is combined with the trend due to intrinsic differences in the dielectric constants of the materials to produce the data shown. Together, the observed trend is quite strong. One could approximate the slope of the trend that is due to hydrophobicity alone by subtracting the slope of the intrinsic data (dry) from that of the wet data. This gives (−0.0293) − (−0.0131) = −0.0162, which is a slightly stronger trend than the dry intrinsic data itself gives. This suggests that the conventionally expected decrease of the ambient dielectric

Table 5. Refractive Index

polymer	TE	TM	TE – TM birefringence
6FDA-PDA	1.5901 ± 0.0035	1.58295 ± 0.004	0.0072
6FDA-FPDA	1.5783 ± 0.0005	1.5756	0.0027
6FDA-DAT	1.5826 ± 0.0002	1.5776 ± 0.002	0.005
6FDA-TFMPDA	1.5528 ± 0.0007	1.5484 ± 0.0006	0.0036
6FDA-2DAT	1.5633 ± 0.0023	1.5586 ± 0.00325	0.0047
6FDA-2TFMPDA	1.5164 ± 0.002	1.5129 ± 0.0019	0.0035
6FDA-TFPDA	1.5481 ± 0.0008	1.5413 ± 0.0008	0.0068
6FDA-OFB	1.5395 ± 0.002	1.5327 ± 0.0038	0.0068
6FDA-22′PFMB	1.5520 ± 0.001	1.5435 ± 0.0002	0.0085
6FDA-33′PFMB	1.5450	1.5258	0.019

constant, that accompanies the incorporation of fluorine into a structure, is due in nearly equal parts (≃50:50) to the change in hydrophobicity and to the combined contribution of the change in molar polarizability and the change in free volume. So, from the standpoint of ambient dielectric behavior, the change in dielectric constant with fluorination that is due to change in hydrophobicity is by far the most important single factor. Apportionment of the trend in the intrinsic (dry) dielectric behavior between changes in free volume and polarization is addressed specifically in two other reports previously mentioned,[24,25] but ranges from 11.5/38.5 to 47.5/2.5.

For want of a rule-of-thumb, on average, the decrease in dielectric constant that usually accompanies fluorine incorporation can be apportioned between these three effects as follows: changes in hydrophobicity (50%), changes in free volume (25%), and changes in total polarizability (25%). The large variation from material to material must, however, be kept in mind.

It is especially significant that the apparent primary role of fluorine in reducing the dielectric constant under ambient conditions is the elimination of water from the polymer. This is because the dipole orientation of water is quite facile and can persist up to high frequencies (10^{13} Hz for free water) and so can play an important role in determining the dielectric performance of materials used in communications and even in ultrashort rise time microelectronic packaging devices. This is in contrast to the dipole reorientation of polymer backbone segments (which increase with nonsymmetric fluorine substitution) that are resonant at such low frequencies, at typical operating temperatures, that they are unlikely to play a significant role in the performance of high-speed packaging devices.

Refractive Index. The refractive indicies in both the in-plane and out-of-plane directions are shown in Table 5. The difference between them, the birefringence, in general shows a negligible degree of preferential orientation. This is expected since the 6FDA unit imparts a substantial kink to the backbone at each repeat unit, making these materials essentially amorphous. The refractive index decreases with increased fluorination due both to the lower bond refractivity of the C–F bond, relative to C–H, and to the somewhat greater free volume that fluorinated analogs usually have relative to hydrogen counterparts. This trend of decreasing refractive index can be seen in the plot of n^2 in Figure 6.

Table 6. Glass and β Transitions[a]

polymer	T_g (tan δ_{max})	T_g (onset)	β
6FDA-PDA	370	354	129(154)[b]
6FDA-FPDA	370	349	159
6FDA-DAT	358	331	177
6FDA-TFMPDA	366	350	230
6FDA-2DAT	379		231
6FDA-2TFMPDA	365	334	265
6FDA-TFPDA	371	345	223
6FDA-OFB	364	337	203
6FDA-22′PFMB	362	334	253
6FDA-33′PFMB	367		232

[a] DMTA, bending 1 Hz. [b] Physical aging, 1 year.

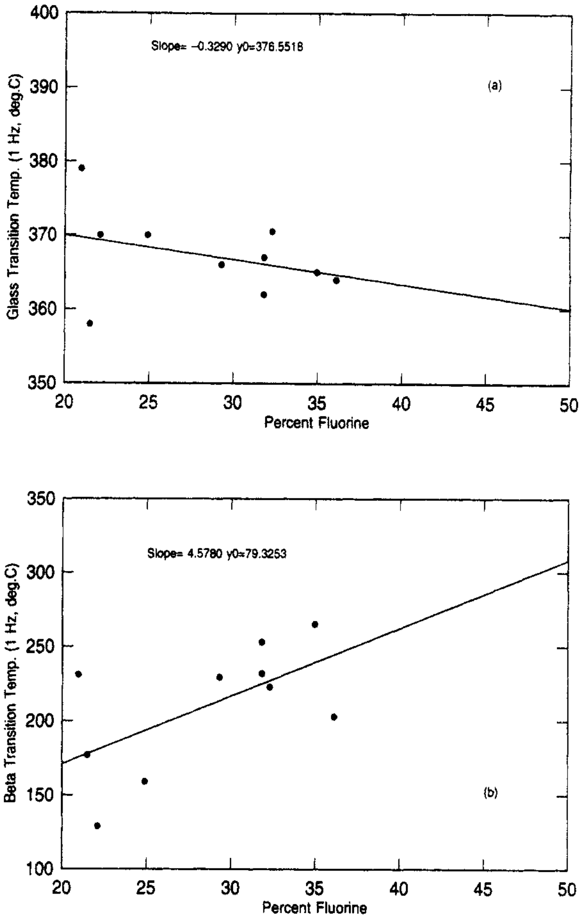


Figure 7. Glass transition versus percent fluorine (a) and β transition versus percent fluorine (b).

Viscoelastic Relaxations. The glass and β relaxation temperatures measured at 1 kHz are shown in Table 6 and Figure 7. It is clear that fluorine substitution does not appreciably affect the glass transition in this series, other than a very slight decline in the average T_g with increasing fluorine content. This is in contrast to the significant reduction in T_g, associated with corresponding weight percent fluorine, when introduced in the form of a long fluorinated side chain.[35] Fluorine substitution does appear, however, to increase β transition temperatures to a substantial degree. It is likely that both the increased steric volume and mass of fluorine contribute to this effect and will be addressed in greater detail in a future report.[36] Increases in the β temperature for 6FDA-PDA with time (129–154 °C over 1 year) may be due to increased intermolecular interaction that accompanies physical aging. Thus, the β process in polyimides may not be entirely local as is often assumed.

Thermal Stability. The dynamic thermogravimetric degradation is summarized in Tables 7 and 8. It can generally be said that there are not dramatic differences in the onset of significant weight loss among the 6FDA-based materials. It would appear that the hexafluoroisopropylidene group is a common thermal weak link leading to relatively minor differences in this series. Although of minor consequence, it is clear that there is a greater discrepancy between the nitrogen and air onset values for the methylated materials, indicating a greater oxidative sensitivity of these groups.

Table 7. Thermal Degradation in Nitrogen

polymer	film	$T_d(2\%)$,[a] °C	$T_d(5\%)$, °C	$T_d(10\%)$, °C
6FDA-PDA	yes	515	535	552
6FDA-DAT	yes	502	521	535
6FDA-TFMPDA	yes	503	523	541
6FDA-2DAT	yes	500	532	551
6FDA-2TFMPDA	yes	520	551	578
6FDA-TFPDA	yes	517	543	568
6FDA-OFB	yes	507	530	558
BPDA-PDA	yes	589	610	626
BPDA-TFPDA	no	575	603	622
PMDA-TFPDA	no	547	575	593
BTDA-TFPDA	no	543	579	601

Table 8. Thermal Degradation in Air

polymer	film	$T_d(2\%)$,[a] °C	$T_d(5\%)$, °C	$T_d(10\%)$, °C
6FDA-PDA	yes	505	525	541
6FDA-DAT	yes	476	506	526
6FDA-TFMPDA	yes	494	513	530
6FDA-2DAT	yes	463	508	538
6FDA-2TFMPDA	yes	505	531	553
6FDA-TFPDA	yes	499	519	539
6FDA-OFB	yes	496	518	536
BPDA-TFPDA	no	557	588	603
BTDA-TFPDA	no	542	572	590

[a] T_d at 2% weight loss.

Conclusions

Polyimides with high degrees of fluorine substitution have been synthesized. Diamines with fluorinated groups in the position ortho to the amino groups were successfully polymerized to high molecular weight utilizing a condensation consisting of a solution polycondensation followed by a solid-state chain extension. In cases of extremely low reactivity, high molecular weight was achieved utilizing a cyclic approach consisting of repeated cure, redissolve, and recast steps.

This polymer series was used to probe several structure/property relationships of interest. It was found that fluorine substitution generally reduced the refractive index and dielectric constant, the latter more strongly in cases with symmetric substitution. It was estimated that around 50% of the observed decreasing trend in the dielectric constant versus percent fluorine can be attributed to a reduction in the absorbed moisture due to an increase in hydrophobicity. The remaining 50% can be apportioned, on average, between increased free volume ($\simeq$25%) and reduced total polarizability ($\simeq$25%). The distribution is material specific however, and the actual values, obtained from work detailed elsewhere,[24,25] range from 11.5/38.5 to 47.5/2.5.

In addition, increased fluorine in the backbone led to only slight overall decreases in the glass transition temperatures but led to significant overall increases in the β transition temperatures. Little effect of fluorine substitution on dynamic thermal or thermooxidative stability was found in this series.

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