Synthesis and properties of some new fluorine-containing polyimides

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Polyimides from 4,4′-hexafluoroisopropylidene diphthalic anhydride and fluorine-containing diamines varying in structure have been prepared in order to study the effect of different fluorinated segments upon the dielectric constant. The thermal and electrical properties of the new polymers are discussed. The effect of fluorine substitution on the dielectric constant of the polyimides has been demonstrated for a broad spectrum of fluorine-containing diamine structures.

(Keywords: polyimides; fluorinated diamines; dielectric constant; thermal stability)

INTRODUCTION

Aromatic polyimides constitute an important class of thermally stable polymers, where a desirable balance of thermal, mechanical and electrical properties required for specific applications has been pursued by varying the macromolecular structure[1–4].

One important application of polyimides is for insulating layers between levels of thin film wiring in high density electronic packaging such as large-scale and very large-scale integrated (LSI and VLSI) circuits[5]. For application as an insulator in packaging, the material must possess good mechanical properties over the processing temperature range, good adhesion, a low thermal expansion coefficient, thermal stability, a glass transition temperature (T_g) higher than the processing temperature, and, most importantly in the context of the work reported here, the dielectric constant must also be as low as possible[6]. Numerous investigators have been engaged in the study of polymers that simultaneously meet all these requirements. An important approach has been to decrease the dielectric constant by incorporating fluorinated segments in the polymers—for example, the versatile hexafluoroisopropylidene group in the diamine and/or in the anhydride used for the polyimide synthesis[7–9]. It has been suggested[8] that the presence of the hexafluoroisopropylidene group in the polymer lowers the dielectric constant by decreasing interchain electronic interactions in the polymer. Other scientists have investigated the effect of fluorinated segments and have extended the useful range of polyimide properties, particularly with respect to dielectric behaviour[10]. The effect of fluorine on the dielectric constant and electrical properties of polyimides has not been investigated in terms of the prevailing mechanism, and the relative contributions of steric effects, electronic polarization, chain packing efficiency and fractional free volume have not been defined for polymers of systematically varied structure, in part because suitable fluorine-containing monomers have not been available for synthesis and systematic studies. Work is in progress on the fundamental aspects of this problem[11]. The work reported here is part of an attempt to broaden the spectrum of fluorine-containing polymers available such that, in principle at least, the role of different fluorine-containing moieties (e.g. aliphatic *versus* aromatic) in lowering the dielectric constant can ultimately be defined for the design of optimal macromolecular structures.

EXPERIMENTAL

Materials

4,4′-(Hexafluoroisopropylidene)diphthalic anhydride, (6FDA), electronic grade, was obtained from Hoechst Celanese Corp. and was used as received. The fluorinated diamines (*Figure 1*) 2,2-bis[4-(difluoro-4-aminophenoxy)phenyl]hexafluoropropane (I), 2,6-diamino-4-trifluoromethylphenyl diperfluorophenylmethyl ether (II), 2,6-diamino-4-trifluoromethylphenyl 2′,2′,3′,3′,4′,4′,4′-heptafluorobutyl ether (III) and (2,5,8-tri-trifluoromethyl-8-3-fluoro-4-aminophenylcarbamoyl-4,7-trioxaheptafluorooctyl) ε (2′,5′-ditrifluoromethyl, 5′-3-fluoro-4-aminophenylcarbamoyl-1′, 4′-dioxa-tetrafluoropentyl) perfluoropentane (IV) were synthesized in this laboratory and are reported elsewhere[12]. Diamines, 1,4-bis-(4-aminophenoxy) tetrafluorobenzene (V) and 4,4′-bis(4-aminophenoxy)octafluorobiphenyl (VI) were prepared according to the reported procedure[13,14]. 2,2-Bis[4-(4-aminophenoxyl)phenyl]hexafluoropropane (BDAF) was obtained from Du Pont and recrystallized from absolute alcohol. *N*-methyl-2-pyrrolidinone (NMP, Aldrich-sure seal) was vacuum distilled over P_2O_5 prior to use.

Preparation of polyimides

In a typical polymerization reaction, a flame-dried three-necked flask with a magnetic stirrer was charged with diamine (I–IV) and NMP under nitrogen, and an equimolar amount of 6FDA followed by NMP were added to reach a 12% (w/v) concentration. The reaction

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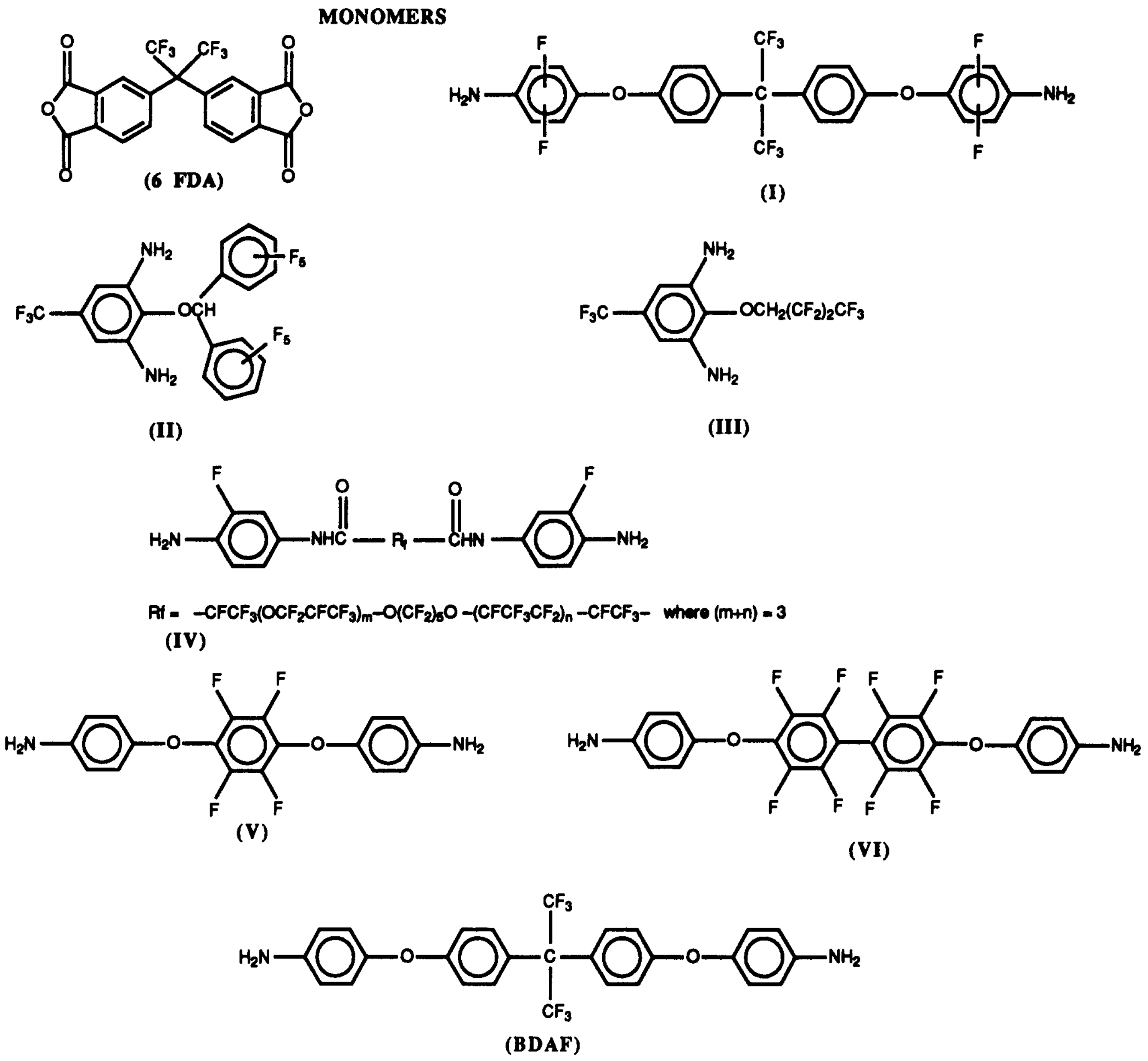

Figure 1 Monomers used

was stirred at room temperature for 24 h. At this stage a sample of polyamic acid was withdrawn for further study. The remaining solution was stirred at 60°C for 5 h, and then at 100°C for another 5 h (heating at higher temperature, i.e. 150°C, resulted in discolouration of the reaction mixture). The polyamic acids from diamines V, VI and BDAF were prepared similarly except that the reaction was carried out at room temperature for 24 h without subsequent heating.

The polyamic acid solutions were filtered to 0.5 μm, cast on a silicon wafer and then heated in a level vacuum oven at 70°C for 12 h followed by 100, 150, 200 and 250°C for 2 h each, and finally at 300°C for 1 h (thermal imidization).

Properties

The Fourier transform infra-red (*FT*i.r.) spectra were obtained by using a BIORAD-60 instrument.

Molecular weights were measured on a Waters-244 GPC with a refractive index detector using tetrahydrofuran as a mobile phase at a flow rate of 1 ml min^{-1}. The Styragel columns connected in series were 10000, 500 and 100 Å. The molecular weights are relative to a polystyrene standard. The thermal response of the polymers was studied on a Stanton Redcroft thermobalance 706 at a heating rate of 10°C min^{-1} and nitrogen flow rate of 50 ml min^{-1}. The T_g was obtained from the inflection point in d.s.c. (Du Pont 1090) at a heating rate of 10°C min^{-1} under nitrogen. The dielectric constant and dissipation factor of the polymer films were measured by an independent laboratory (Matech Associates, Scranton, PA, USA) at room temperature, 100, 250 and 300°C, using a set of Rutherford Research parallel plate micrometer electrodes (model 1592-2T) at 100 kHz. Samples were preconditioned at 22°C and 50% relative humidity (r.h.). Humidity-induced changes in the dielectric constant of experimental polyimide films at 10 kHz–1 MHz have been reported[15] and dielectric measurements have been used to calculate the relative polarizability of absorbed water. As humidity-induced

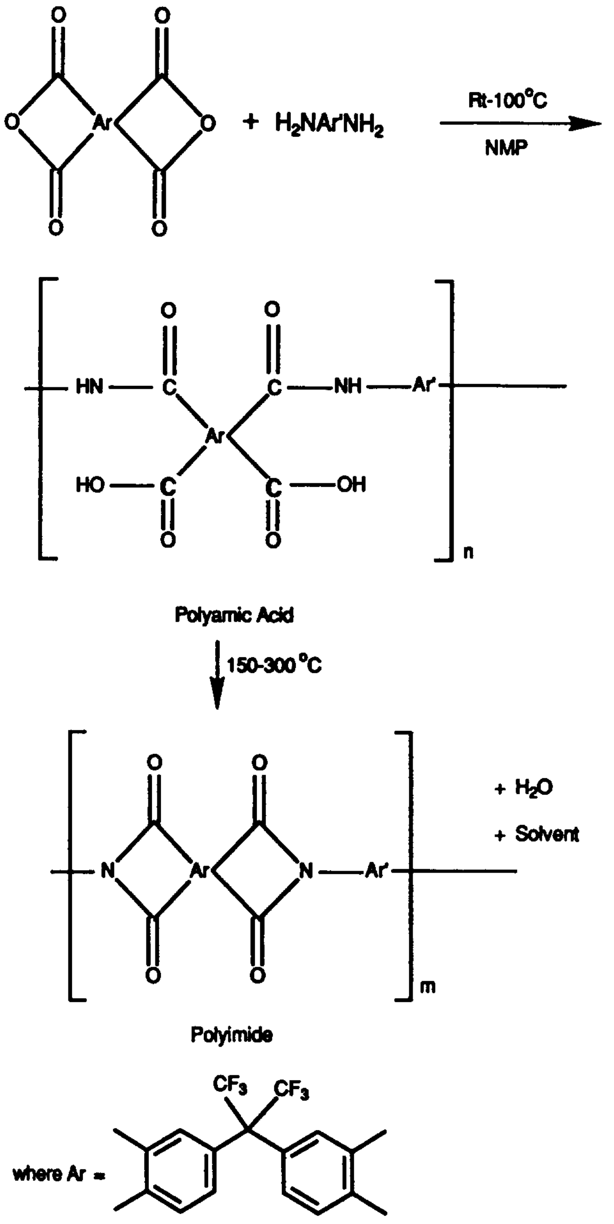

Figure 2 Synthesis scheme for polymerization. $H_2NAr'NH_2$ represents the various fluorinated diamines as synthesized

changes have been shown to be appreciable, a need exists for establishing a standard humidity condition for reporting dielectric constants. Many authors have used 50% r.h. and we chose to follow this trend.

RESULTS AND DISCUSSION

The polymerization reactions of the fluorinated diamines with 6FDA proceeded as illustrated in *Figure 2*, yielding the polyamic acids. After the room temperature reaction, the polyamic acids from diamines V, VI and BDAF were highly viscous, whereas in the case of diamines I–IV there was no appreciable increase in solution viscosity. The solution viscosity of the polyamic acids from diamines I, III and IV increased to a reasonable extent after heating at 100°C.

All polyamic acids gave clear transparent films after thermal imidization (except for those from diamines I and II, which were not self-supporting). The polyimides were soluble in NMP, ethyl acetate and acetone (except for that from diamine II).

The *FT*i.r. spectra of the polyimides showed characteristic absorptions in the regions 1775–1785, 1715–1725, 1340–1365 and 705–735 cm^{-1}. The former two bands are commonly attributed, respectively, to the symmetric and asymmetric stretching of the carbonyl groups coupled through the five-membered ring. The assignments for the remaining two bands are less certain. The band in the 1340–1365 cm^{-1} region has been attributed to the C–N stretch. In all the imidized samples the absence of absorption at 3000–3500 cm^{-1} (where $>$NH and $>$OH absorbs) is taken as evidence that the samples were essentially fully imidized.

The molecular weights of the polymers obtained from g.p.c. are given in *Table 1*. They are reasonable for polyimides obtained from diamines IV–VI, marginal in the case of polymers from diamines I and III and low in the case of the polyimide prepared from diamine II. This may be due to decreased nucleophilic reactivity of the amine caused by the presence of a strong electron-

Table 1 Physical and dielectric properties of fluorine-containing polyimides

Diamine used in polyimide[a] (%F in polyimide)	Reaction temp. (°C) (film forming)	Molecular weight			Dielectric constant, at (100 kHz)			
		$\bar{M}_w$	$\bar{M}_n$	$\bar{M}_w/\bar{M}_n$	Room temp.	100°C	250°C	300°C
I (19.03)	100 (No)	9949	3964	2.5	–	–	–	–
II (26.10)	100 (No)	807	417	1.94	–	–	–	–
III (38.87)	100 (Yes)	17 604	8507	2.07	2.93	2.98	2.90	3.08
I4 (48.06)	100 (Yes)	55 372	29 297	1.89	2.93	2.91	2.82	3.00
V (24.61)	RT[b] (Yes)	29 805	15 602	1.91	2.83	2.81	2.89	2.95
VI (31.73)	RT (Yes)	58 347	30 402	1.92	2.78	2.79	2.82	2.95
BDAF (24.62)	RT (Yes)	78 386	27 600	2.84	2.96	2.90	2.89	2.99

[a] Dianhydride used: 6FDA
[b] Room temperature

Table 2 Thermal behaviour of fluorine-containing polyimides

Diamine used in polyimide[a]	Reaction temp. (°C)	T_g (in nitrogen) by d.s.c. (°C)	Thermal decomposition (in nitrogen) (°C)[b]				
			T_{b_1}	T_{e_1}	T_{b_2}	T_{e_2}	Residue at 600°C (%)
I	RT	–	508	627	–	–	62
	100	224.0	505	625	–	–	63
II	RT	–	321	450	504	592	60
	100	321.7	353	490	513	584	63
III	RT	–	425	485	530	630	48
	100	227.0	425	475	540	605	48
IV	100	116.3	355	396	526	605	26
V	RT	243.8	505	630	–	–	66
VI	RT	271.2	518	660	—	—	76
BDAF	RT	231.7	512	635	–	–	66

[a] Dianhydride used: 6FDA

[b] T_b, temperature of extrapolated beginning of weight loss; T_e, temperature of extrapolated end of weight loss

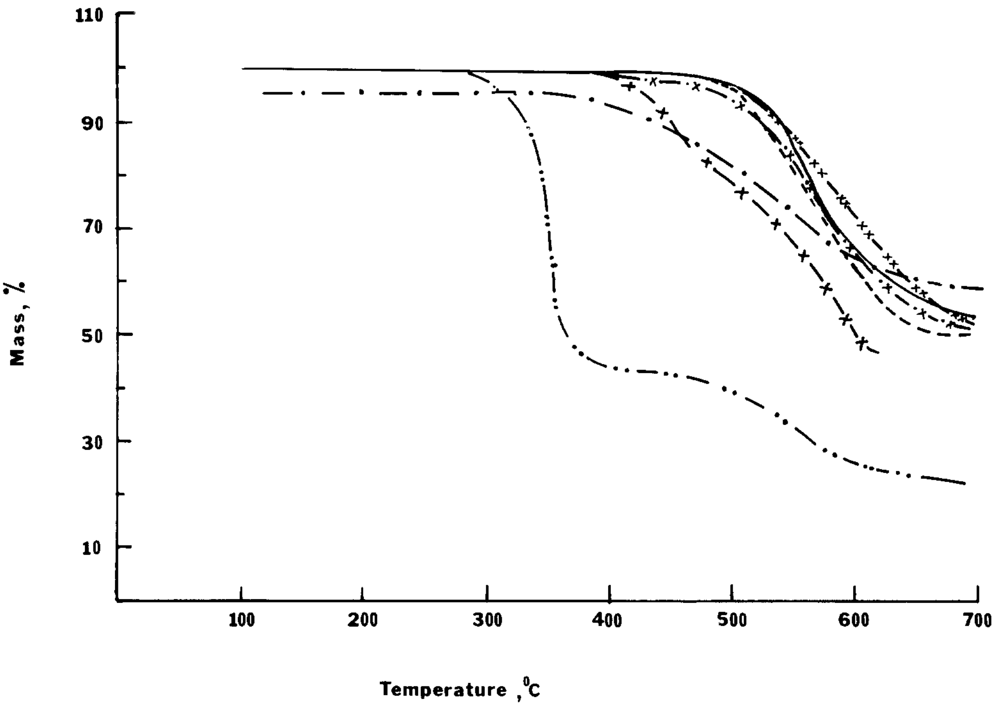

Figure 3 Thermogravimetric curves of polyimides in nitrogen: (——) BDAF; (— —) I; (—·) II; (—×) III; (—··) IV; (—·×) V; (—××) VI

withdrawing group *ortho* to the amino group (fluoro substituent in I, and fluorinated aryloxy or alkoxy groups in II and III, respectively). In addition to this electronic effect, steric hindrance due to the presence of a bulky group *ortho* to the amino groups may also lower reactivity, causing a decrease in molecular weight, as in the case of the polyimide from diamine II.

Predictably, the thermal response of the polyimides (*Table 2*, *Figure 3*) was dependent upon the structure of the diamine (as the dianhydride moiety is the same throughout). Thus, the polyimide from diamines I, V and VI showed a single step weight loss similar to that observed in the case of BDAF in the temperature range 500–600°C, whereas in the polymers from diamines II–IV, a two-step weight loss, the first step occurring in the 320–495°C temperature range and the second in the 500–630°C temperature range, was observed (*Table 2*). In all instances, there was no weight loss at ~200–250°C suggesting the absence of solvent and complete imidization. (Further imidization, if any, would probably occur above the T_g.)

The polyimides prepared from diamines I, V and VI are thermally stable and as expected, the least stable polymer was obtained from diamine IV. High thermal stability has also been observed by Scola *et al.*[7] in the study of thermal response of polymers containing the hexafluoroisopropylidene group.

The thermal stability of polyimides from diamines V and VI is attributed to the aromatic character of the polymers. In all cases 50–70% residue remained at 600°C, except for the polyimide from diamine IV. Further, *Table 2* shows little difference in the overall thermal stability of polyimides prepared from polyamic acids synthesized at different temperatures.

Incorporation of fluorinated substituents in the polyimide results in a considerable effect on the T_g, which is

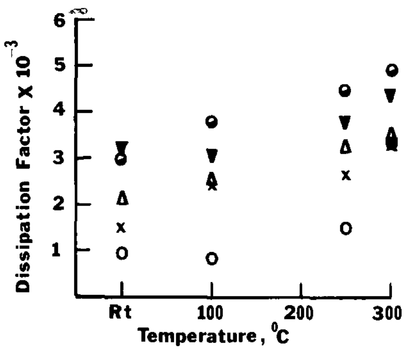

Figure 4 Dissipation factor of polyimide films at various temperatures (Rt, room temperature): (○) VI; (×) V; (△) BDAF; (●) IV; (▼) III

related to the structure of the diamine. Thus, the polyimides from I (containing two hexafluoroisopropylidene groups) and III (with fluoroalkoxy groups) exhibit low T_g (~225°C). The polyimide from diamine II (in contrast to that from III) had a T_g of 322°C, presumably due to barriers to molecular rotation in the presence of bulky phenyl groups in proximity to amino groups. The T_gs of the polyimides from diamines V and VI were relatively low (240 and 270°C, respectively) probably due to the flexibility imparted by ether linkages. As expected, the polyimide from diamine IV containing a perfluoroalkyl ether chain had the lowest T_g (*Table 2*).

The dielectric constant and dissipation factor for these materials at 100 kHz varied from 2.78 to 3.08 and 0.00097 to 0.0049, respectively, in the temperature range studied (*Table 1*, *Figure 4*), the lowest values being for the polyimide prepared from diamine VI. In all cases an increase in dielectric constant was noted at 300°C for these polymers due to the increased molecular mobility at this temperature which is higher than the T_g (*Table 2*). A similar behaviour was observed by Hougham *et al.* for the 6FDA-octafluorobenzidine polyimide[10].

Previous investigators have reported a decrease in the dielectric constant of fluorine-containing polyimides as compared to fluorine-free polymers. In most instances, the fluorine incorporated in the polymers has been derived from the hexafluoroisopropylidene group. The effect of fluorine present as a substituent in aromatic rings has been studied[10,11], and the effect of perfluoroalkoxy substituents has been recently reported[16]. In the latter case, an attempt has been made to provide a correlation between the dielectric constant at 1 kHz to fluorine content for a series of polymers. In the case of data summarized in *Table 1*, correlation of the dielectric constant to fluorine content would have limited value because of the lack of systematic variation in the polymer structures. However, the data suggest that at comparable fluorine content, fluorine bound to aromatic rings is more effective in lowering the dielectric constant than aliphatic fluorine (e.g. polyimides from V and VI *versus* BDAF).

It is evident from the results reported to date that several factors contribute to the decrease in the dielectric constant observed in several polyimide systems. Some of these factors have been discussed previously by us and by others, and they include the following considerations:

1. The presence of bulky groups between imide linkages may reduce interchain electronic interaction thus decreasing the dielectric constant.
2. The presence of fluoro substituents may cause steric changes, resulting in a less efficient chain packing and an increase in the free volume of the polymer, bringing the dielectric constant closer to the value of air.
3. Fluorine may effect a decrease in the electronic polarizability due to its strong electron-withdrawing inductive effect, thus decreasing the dielectric constant.

In contrast to this, the strong electron-attracting force caused by the high electronegativity of the fluorine atom can produce an additional dipole moment, thus increasing the orientational component of the polarization and hence increasing the dielectric constant. In the case of polyimides from diamines V and VI this is of no consequence in itself to the overall dipole moment of the monomer unit as the C–F bonds are symmetrically placed on phenyl rings. In other polyimides (from diamines III, IV and BDAF) it may increase the overall dipole moment, and this may account for the higher dielectric constant in polyimides from diamines III, IV and BDAF as compared to those from V and VI, even though the fluorine content is higher in the former case.

The effect of moisture absorption in polymers of varying structure and fluorine content on the dielectric constant must also be considered.

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