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Synthesis of Fluorinated Polyimides

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I. INTRODUCTION

Polyimide materials have been extensively used in the aerospace and electronics fields because they are thermally stable, mechanically strong, and electrically insulating [1-3]. These fields also need transparent polyimide materials to cover solar cells and polyimides that have low permittivity to decrease the delay time of electrical circuits. Optoelectronics needs polyimide materials with transparency at wavelengths longer than those of the visible light region and a controllable refractive index. One of the most effective ways to satisfy these needs is to introduce fluorine into polyimide materials [4,5]. Fluorinated polymers, such as poly(tetrafluoroethylene), have attractive features such as low water uptake, water and/or oil repellence, low permittivity, low refractive index, resistance to wear and abrasion, and both thermal and chemical stability. The fluorine atom inducing these properties is the second smallest atom, and its 2s and 2d electrons are close to the nucleus. Its electric polarity is therefore small, and it is the most electronegative of all the elements. This high electronegativity results in strong bonds between carbon and fluorine atoms, giving fluorocarbon materials high thermal and chemical stability. The low polarity of fluorine gives fluorocarbons a low refractive index and low dielectric constant, and the low cohesive energy and surface free energy due to the low polarity result in a low uptake of water, water and oil repellence, and resistance to wear and abrasion. The introduction of fluorine atoms into polyimides is therefore expected to produce polyimides with many attractive features. However, there is also a danger that the resultant polyimides may have some undesirable properties such as low adhesion strength, low mechanical strength, or a high coefficient of thermal expansion(CTE). The goal of fluorinated polyimide research is to obtain the advantages of introducing fluorine atoms without sacrificing the many advantages of polyimides.

In 1972 Critchley et al. reported on the synthesis and properties of polyimides bonded with perfluoroalkylene moieties [6,7]. They synthesized fluorinated polyimides in two ways: by solution polymerization and by melt polymerization. Figure 1 shows the synthesis scheme for one of the perfluoroalkylene-linked polyimides. Melt polymerization, which is carried out by fusion of diamine and dianhydride, has the advantage of shortening the synthesis path, but it

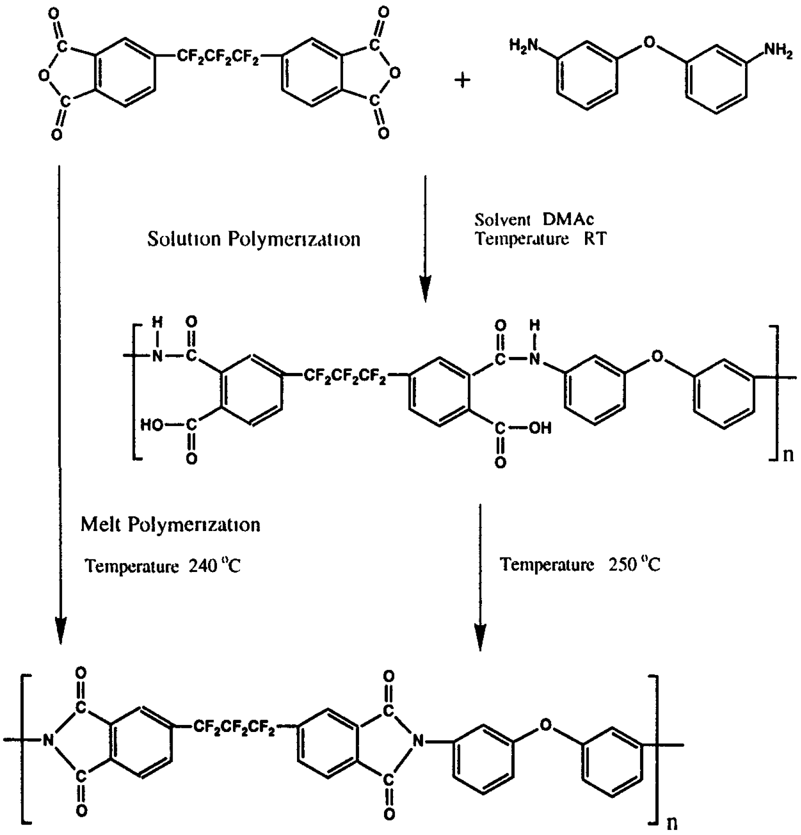


Figure 1 Synthesis scheme for Critchley's fluorinated polyimide. (From Ref 6)

is restricted to a narrow range of fusible diamines and dianhydrides Solution polymerization, on the other hand, can synthesize the whole range of polyimides

In the 1980s, polyimides prepared from 2,2-bis(3,4-dicarboxyphenyl) hexafluoropropane dianhydride (6FDA) were reported by other researchers [5,8–11] The 6FDA polyimides, which can be synthesized through conventional solution polymerization (Fig. 2), have good transparency [9], and have lower dielectric constants than those prepared from other nonfluorinated dianhydrides [11].

Many researchers have recently been investigating the next generation of fluorinated polyimides for electronics and optoelectronics applications For electronics, there are two trends in the development of fluorinated polyimides. One is to make the dielectric constant as low as possible, and the other is to introduce fluorine atoms while maintaining many of the advantages of polyimides. Fluorinated polyimides have recently attracted attention for optoelectronics because optical polymers require thermal stability as well as transparency, and fluorinated polyimides have the possibility to fulfill these requirements

This chapter reviews recent developments in fluorinated polyimides for electronics and optoelectronics with particular emphasis on their synthesis.

A number of diamines and dianhydrides are mentioned. For easier comprehension, we have listed their chemical structures and abbreviations. Tables 1–4 show fluorinated dianhy-

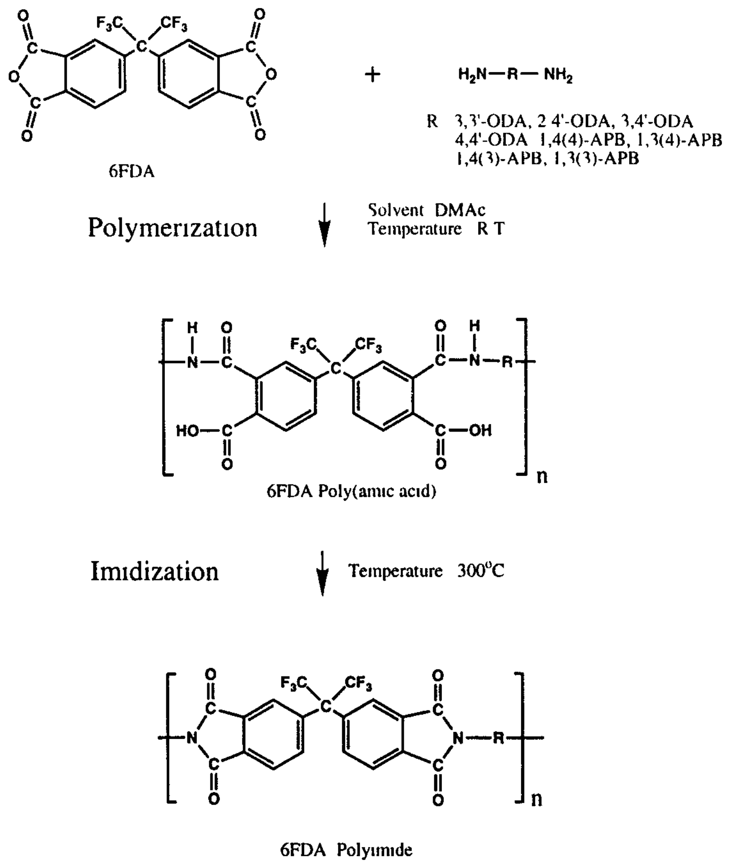


Figure 2 Synthesis scheme for 6FDA polyimide (From Ref 9)

drides, nonfluorinated dianhydrides, fluorinated diamines, and nonfluorinated diamines, respectively.

II. FLUORINATED POLYIMIDES FOR ELECTRONICS

When a polyimide is used as an insulating material, the speed of signal transmission in the electrical circuit increases as the dielectric constant of the polyimide decreases, because the delay time of an electrical circuit is proportional to the square root of the dielectric constant of the insulating material. A low dielectric constant is the most attractive property of polyimide materials for electronics applications Introducing fluorine atoms into polyimides is one of the most efficient ways to obtain this In this case, it is important to achieve the low dielectric constant while maintaining many of the advantages of polyimides such as high thermal stability and mechanical strength.

In this section we describe novel fluorinated polyimides derived from new fluorinated diamines or dianhydrides invented after the 6FDA polyimides.

For easy comprehension, the characteristics of the fluorinated polyimides in each subsection are shown in similarly formatted tables that show the monomers used, imidization conditions, poly(amic acid) (PAA) viscosity, molecular weight, film formation, and dielectric constant.

Table 1 Chemical Structures of Fluorinated Dianhydrides

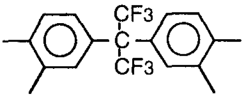
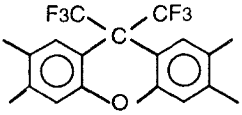
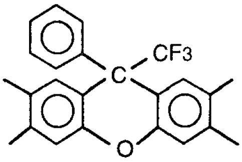
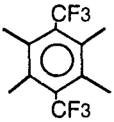
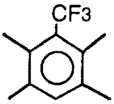
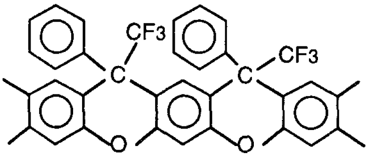
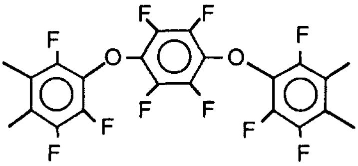
Chemical structure	Abbreviation
	6FDA
	6FCDA
	3FCDA
	P6FDA
	P3FDA
	PXPXDA
	10FEDA

Table 2 Chemical Structures of Nonfluorinated Dianhydrides

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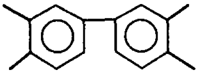
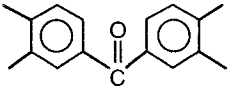
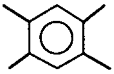
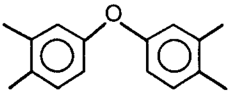
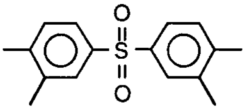
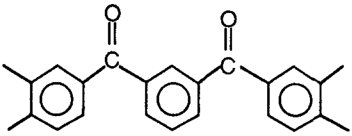
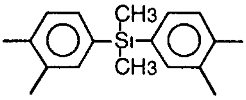
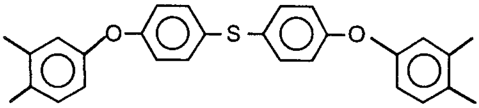
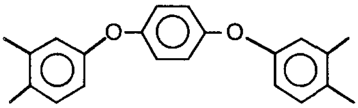
	BPDA
	BTDA
	PMDA
	ODPA
	DSDA
	IDPA
	SiDA
	BDSDA
	HQDEA

Table 3 Chemical Structures of Fluorinated Diamines

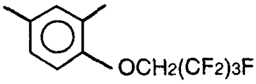
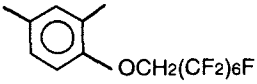
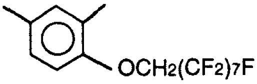
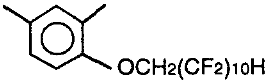
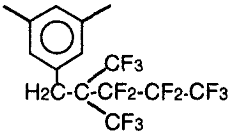
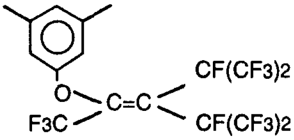
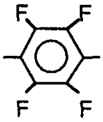
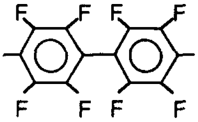
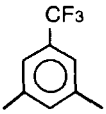
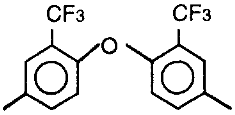
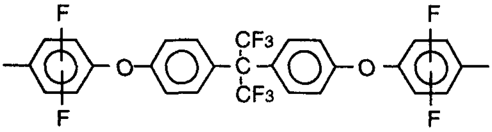
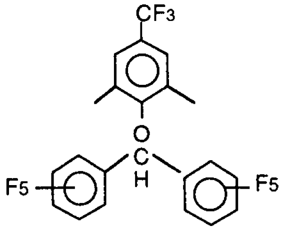
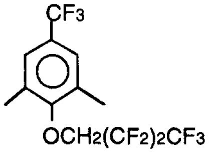
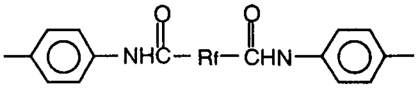
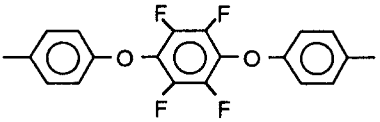
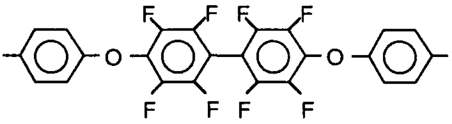
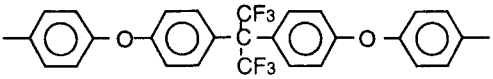
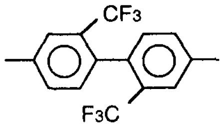
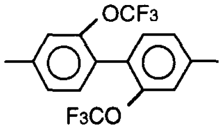
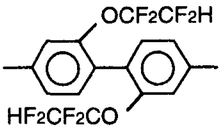
Chemical structure	Abbreviation
	7FMDA
	13FMDA
	15FMDA
	20FMDA
	RfbMPD
	PFDA
	TFPDA
	OFB
	35-DABTF
	124-OBABTF
	4FBDAF

Table 3 Continued

Chemical structure	Abbreviation
	DTDE
	DTHE
 $R_f = -CFCF_3(OCF_2CFCF_3)_m-O(CF_2)_5O-(CFCF_3CF_2)_n-CFCF_3-$ where $(m+n) = 3$	TFATFDADP
	BAT
	BAO
	BDAF
	TFDB
	TFMOB
	TFEOB

(continued)

Table 3 Continued

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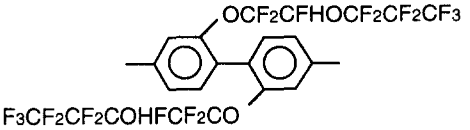
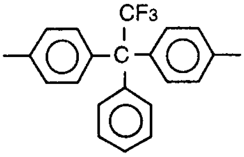
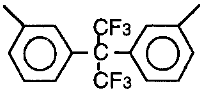
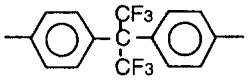
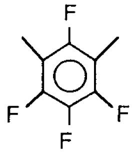
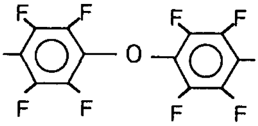
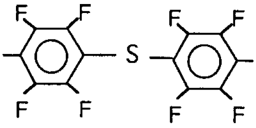
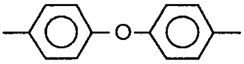
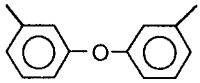
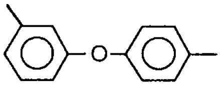
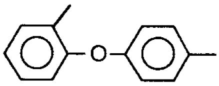
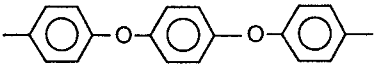
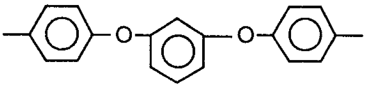
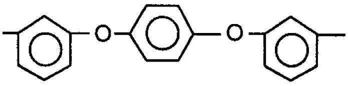
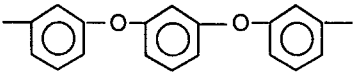
	DFPOB
	3Fdiamine
	3,3′-6F
	4,4′-6F
	4FMPDA
	8FODA
	8FSDA

A. Fluorinated Polyimides with a Pendant Fluorinated Group

Ichino et al [12] synthesized novel fluorinated polyimides containing a fluorinated alkoxy side chain in order to achieve a low dielectric constant They first synthesized four novel fluorinated alkoxy diamines. Figure 3 shows their synthesis routes Fluorinated dinitro-compounds, which were synthesized by the etherification of fluorinated alcohols and 2,4-dinitrofluorobenzene in Et_3N/*N*,*N*-dimethylacetamide (DMAc) at room temperature for 2 h, were reduced with $SnCl_2$/HCl to obtain the four fluorinated alkoxy diamines

Figure 4 shows the synthesis scheme for these polyimides PAA synthesis was carried out in *N*-methyl-2-pyrolidone (NMP) at 25 °C PAA solution was cast onto a glass plate and then heated at 100°C for 1 h, 200°C for 1 h, and 350°C for 1 h to obtain polyimide film Table 5 shows the characteristics of these fluorinated polyimides The inherent viscosities of these

Table 4 Chemical Structures of Nonfluorinated Diamines

Chemical structure	Abbreviation
	4,4′-ODA
	3,3′-ODA
	3,4′-ODA
	2,4′-ODA
	1,4(4)-APB
	1,3(4)-APB
	1,4(3)-APB
	1,3(3)-APB
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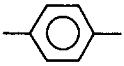
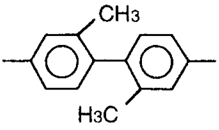
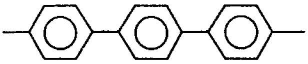
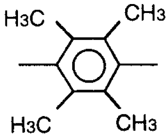
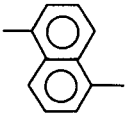
	PDA
	DMDB
	DPTP
	DAD
	1,5-DAN

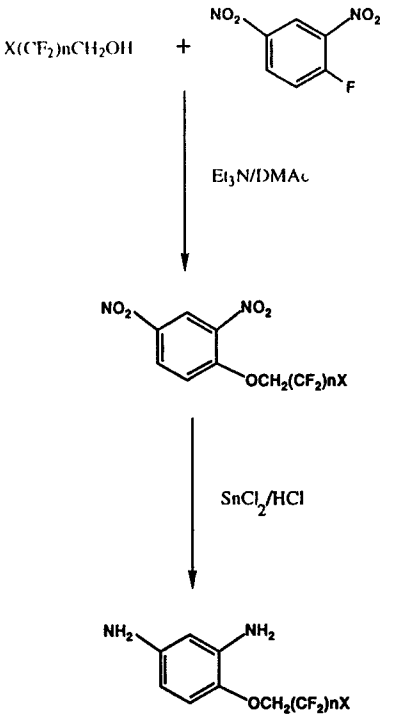


Figure 3 Synthesis route for fluorinated alkoxy diamines X = F, n = 3 7FMDA, X = F, n = 6 13FMDA, X = F, n = 7 15FMDA, X = R, n = 10 20 FMDA (From Ref 12)

poly(amic acid)s are relatively low and tend to decrease with increasing length of the fluorinated alkoxy group There are two causes for this behavior One is a reduction in nucleophilic reactivity of fluorinated diamines by the strong electron-attracting force of a fluorinated alkoxy group, and the other is steric hindrance of the reaction of the adjacent amino group in the fluorinated diamines by the bulkiness of the fluorinated alkoxy group.

The dielectric constant of the polyimides at 1 kHz decreased with increasing fluorine content as shown in Figure 5 The lowest dielectric constant measured was 2 6. The polyimide with the highest fluorine content exhibited low water absorption, so the stability of its dielectric constant was good After aging at 25°C in a relative humidity of 70% for 5 days, the increase in dielectric constant was only 0 1 But the polyimide with this dielectric constant had relatively poor thermal stability its glass transition temperature was 189°C and the polymer decomposition temperature giving 10% weight loss was 455°C This shows that the introduction of a long fluorinated alkoxy group into polyimides lowers the dielectric constant, but also lowers the thermal properties

Auman et al. [13] have reported the synthesis of polyimides with a pendant bis(trifluoromethyl)heptafluoropentyl group They synthesized a novel fluoroalkylated diamine (RfbMPD) that had good reactivity and thermal stability as well as a high fluorine content Figure 6 shows the synthesis scheme for the amine.

Figure 7 shows the synthesis scheme for the polyimides with a pendant bis(trifluoromethyl)heptafluoropentyl group. Table 6 shows the characteristics of the fluorinated polyimides.

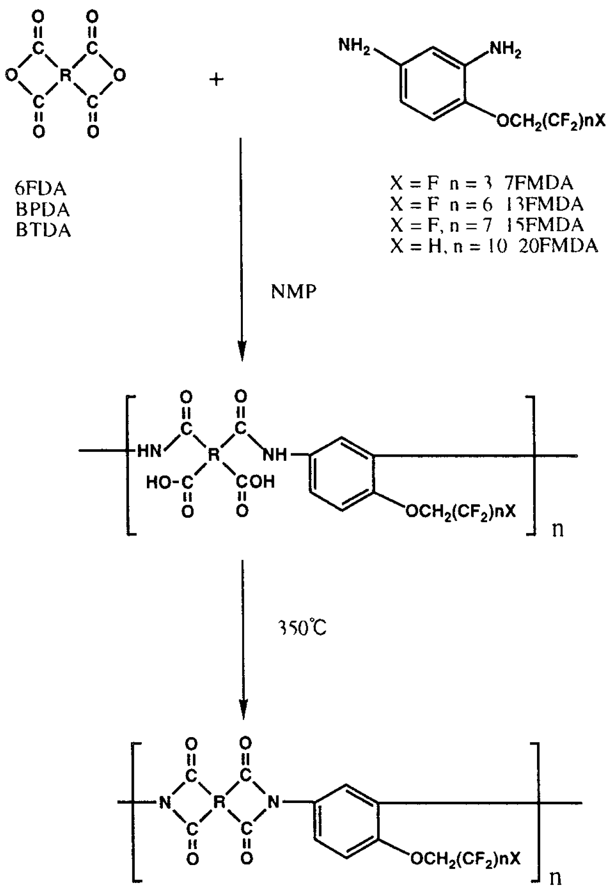


Figure 4 Synthesis scheme for fluorinated polyimides with fluorinated alkoxy side chain (From Ref 12)

The RfbMPD was reacted with several fluorinated and nonfluorinated dianhydrides to form poly(amic acid)s in the conventional way Then the poly(amic acid)s were converted into the polyimides by thermal or chemical imidization Their characteristics are shown in Table 6 These polyimides had a relatively high molecular weight and low dielectric constant In particular 6FCDA/RfbMPD had a high glass transition temperature, at 347°C, as well as a very low dielectric constant, 2 3 at 1 MHz The CTE, however, was high for polyimide, probably a result of the bulky pendant fluorocarbon chain The polyimides with a pendant bis(trifluoromethyl)heptafluoropentyl group are interesting because they have both a low dielectric constant and high glass transition temperature

Yusa et al [14] have reported the synthesis of polyimides with a perfluorononenyloxy group Figure 8 shows the synthesis scheme for the fluorinated polyimides Table 7 shows their characteristics A new monomer, 1,3-diamino-5-(perfluorononenyloxy)benzene (PFDA) was reacted with dianhydrides in the conventional way to form PAAs and converted these into polyimides by heating at 250–300°C The inherent viscosities of the PAAs were relatively low,

Table 5 Characteristics of Fluorinated Polyimides

Monomers						
Dianhydride	Diamine	Imidization conditions Solvent, temperature(°C)/time (h)	PAA viscosity[a] (η[dl/g])	Molecular weight	Film formation	Dielectric constant[b]
6FDA	MPD	NMP, 100/1, 250/1, 350/1	0 70	—	Yes	3 0
6FDA	7FMDA	NMP, 100/1, 250/1, 350/1	0 38	—	Yes	2 9
6FDA	13FMDA	NMP, 100/1, 250/1, 350/1	0 31	—	Yes	2 7
6FDA	15FMDA	NMP, 100/1, 250/1, 350/1	0 33	—	Yes	2 6
6FDA	20FMDA	NMP, 100/1, 250/1, 350/1	0 29	—	Yes	2 6
BPDA	MPD	NMP, 100/1, 250/1, 350/1	0 93	—	Yes	3 5
BPDA	7FMDA	NMP, 100/1, 250/1, 350/1	0 47	—	Yes	3 2
BPDA	13FMDA	NMP, 100/1, 250/1, 350/1	0 32	—	Yes	3 0
BPDA	15FMDA	NMP, 100/1, 250/1, 350/1	0 34	—	Yes	3 0
BPDA	20FMDA	NMP, 100/1, 250/1, 350/1	0 25	—	Yes	3 0
BTDA	MPD	NMP, 100/1, 250/1, 350/1	0 72	—	Yes	3 5
BTDA	7FMDA	NMP, 100/1, 250/1, 350/1	0 41	—	Yes	3 3
BTDA	13FMDA	NMP, 100/1, 250/1, 350/1	0 30	—	Yes	3 0
BTDA	15FMDA	NMP, 100/1, 250/1, 350/1	0 30	—	Yes	2 9
BTDA	20FMDA	NMP, 100/1, 250/1, 350/1	0 28	—	Yes	2 9

[a] Inherent viscosities were measured with 0 5 wt% NMP solution at 30°C

[b] Measurements were made at 23°C, 50% RH, and 1 kHz

Source Ref 12

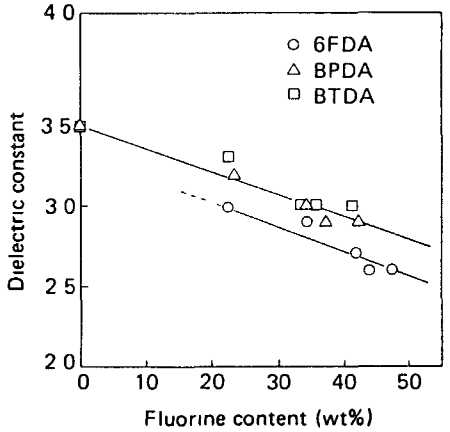


Figure 5 Relationship between dielectric constant at 1 kHz and the fluorine content of fluorinated polyimides and the reference nonfluorinated polyimides. (From Ref. 12.)

0.17 dl/g, because of the low reactivity of PFDA due to its strong electron-withdrawing characteristic. The dielectric constant of 6FDA/PFDA was low, 2.5 at 10 kHz.

Making polyimides with a pendant fluorinated group is a useful way to obtain polyimides with a high fluorine content. By choosing a fluorinated group, one can obtain fluorinated polyimides with a high molecular weight, and such polyimides have both a low dielectric constant and a high glass transition temperature. However, they have the disadvantage of having a high CTE because of the bulkiness of the pendant group.

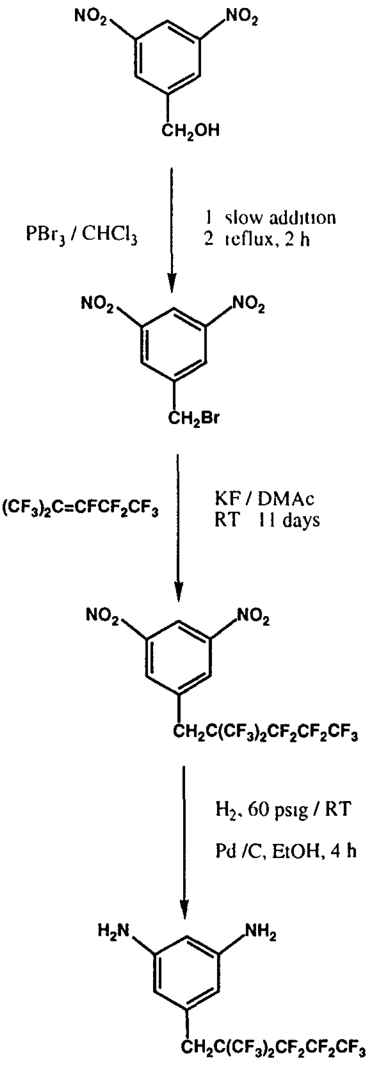
B. Fluorinated Polyimides Prepared from Bis(trifluoromethyl)diaminobiphenyl

2,2′-bis(trifluoromethyl)-4,4′-diaminobiphenyl (TFDB) is interesting as a monomer of fluorinated polyimides. TFDB, whose synthesis route is shown in Figure 9, was synthesized by Maki and Inukai in 1972 [15].

Matsuura et al. [16] synthesized fluorinated polyimides from TFDB and 6FDA or pyromellitic dianhydride or PMDA in the conventional way (Fig. 10). Table 8 shows the characteristics of the fluorinated polyimides from TFDB. They had high intrinsic viscosities. 6FDA/TFDB had excellent properties such as low dielectric constant (2.8 at MHz) and high transparency, and PMDA/TFDB had a low CTE (-0.5×10^{-5} °C^{-1}). 6FDA/TFDB is discussed as an optical material in Sec. III.B.

6FDA/TFDB has another characteristic: it is soluble in common polar organic solvents, such as acetone or tetrahydrofuran. Matsuura et al. used ^{1}H nuclear magnetic resonance (NMR) to characterize the imidization process and found that the imidization reaction began at just over 70°C and was completed by about 200°C.

Ando et al. [17] obtained more detailed information about the molecular structure of 6FDA/TFDB poly(amic acid)s and polyimides during imidization under various conditions by measuring ^{13}C NMR. Figure 11 shows ^{13}C NMR proton-decoupled spectra of 6FDA/TFDB samples cured at various temperatures. Small peaks originating from polyimide are seen in the 70°C sample because the imidization reaction begins at just over 70°C. Significant changes are caused



RfbMPD

Figure 6 Synthesis scheme for RfbMPD (From Ref 13)

by imidization at 120°C. The chemical shifts of the two signals resonated at right (shown by arrows) are the same as those of TFDB. This means that depolymerization of the poly(amic acid) main chain occurred at 120°C. Figure 12 shows the viscosity coefficients of 15 wt% DMAc solutions of 6FDA/TFDB cured under the same conditions as the samples for NMR measurements. The low viscosity of the 120°C sample is consistent with the depolymerization at the poly(amic acid) amid group and decrease of molecular weight identified in the NMR analysis Viscosity increases monotonically with curing temperatures from 120°C to 300°C. This shows that the polycondensation reaction proceeds and the molecular weight of polyimide increases even after imidization is completed (at 200°C)

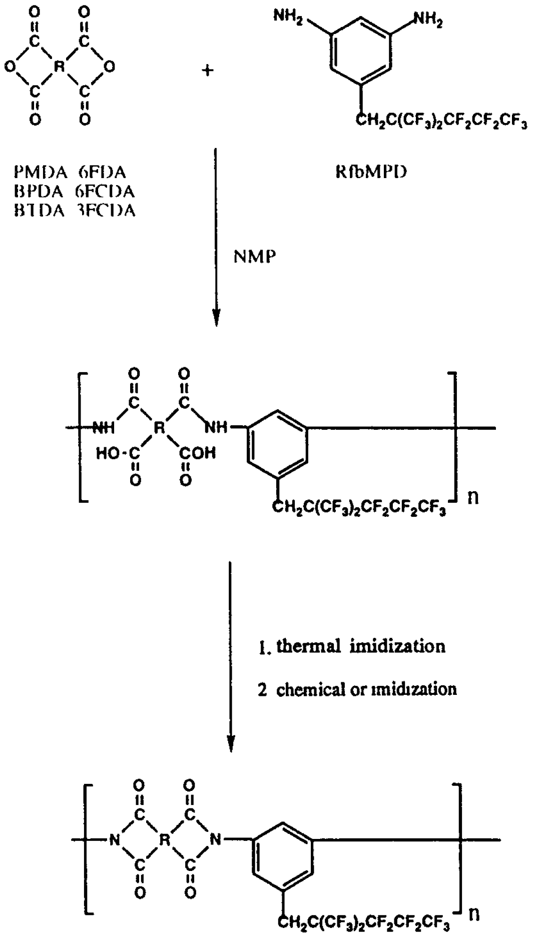


Figure 7 Synthesis scheme for fluorinated polyimides with a pendant bis(trifluoromethyl)heptafluoropentyl group (From Ref 13)

Harris et al. [18–20] have investigated rigid soluble fluorinated polyimides from TFDB and various dianhydrides, PMDA, (BTDA), ODPA, DSDA, 6FDA, and BPDA using a one-step procedure Figure 13 shows the synthesis scheme for the fluorinated polyimides, and Table 9 shows their characteristics The polymerization was carried out in refluxing m-cresol containing isoquinoline Under these conditions the intermediate poly(amic acid)s spontaneously cyclized to the corresponding polyimides Except for PMDA/TFDB, all the polyimides were soluble in *m*-cresol. Their inherent viscosities were from 1 0 to 4.9 dl/g

C. Fluorinated Polyimides Prepared from Perfluoro Aromatic Diamines

Hougham and Tesoro [21] have reported the synthesis and properties of polyimides from perfluoro aromatic diamines The aim of their study was to obtain polyimides with a high glass transition temperature and low dielectric constant for use as an insulator

Table 6 Characteristics of Fluorinated Polyimides

Monomers		Imidization conditions	PAA viscosity	Molecular	Film	Dielectric
Dianhydride	Diamine	Solvent, temperature(°C)/time(h)	(η[dl/g])	weight	formation	constant[c]
PMDA	RfbMPD	NMP, 135/0.5, 200/0.5, 350/1	—	50,800[a]	Yes	3.2
PMDA	RfbMPD	NMP, 135/0.5, 200/0.5, 350/1	—	92,100[a]	Cracked	—
BPDA	RfbMPD	NMP, 135/0.5, 200/0.5, 350/1	—	56,000[a]	Cracked	—
BTDA	RfbMPD	NMP, 135/0.5, 200/0.5, 350/1	—	31,500[a]	Yes	—
6FDA	RfbMPD	NMP, 135/0.5, 200/0.5, 350/1	—	82,700[a]	Yes	—
6FDA	RfbMPD	NMP/acetic anhydride/pyridine (chemical)	—	47,500[a]	Yes	2.7
6FCDA	RfbMPD	NMP/acetic anhydride/pyridine (chemical)	—	53,200[b]	Yes	2.3
3FCDA	RfbMPD	NMP/acetic anhydride/pyridine (chemical)	—	122,000[a]	Yes	2.5

[a] Number-average molecular weights by GPC of PAA in DMAc/LiBr/H_3PO_4/THF at 35°C

[b] Number-average molecular weights by GPC of polyimide in DMAc at 135°C

[c] Measurements were made at 0% RH and 1 MHz

Source Ref 13

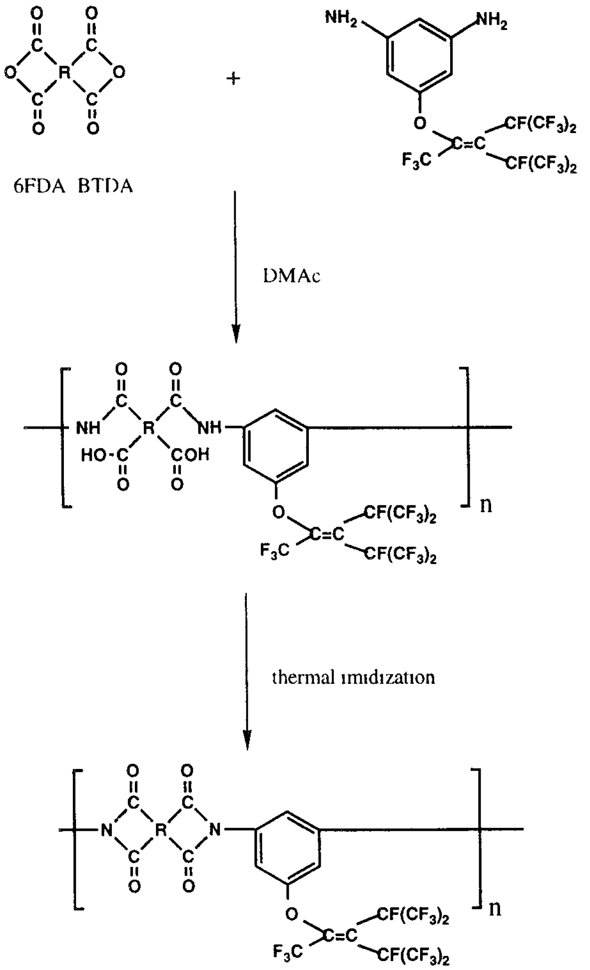


Figure 8 Synthesis scheme for fluorinated polyimides with a pendant perfluorononenyloxy group (From Ref 14)

The perfluoro aromatic diamines they used were 1,4-tetrafluorophenylene diamine (TFPDA) and 4,4′-octafluorobenzidine (OFB) In all the polyimides obtained using the perfluoro aromatic diamines, only low-molecular-weight oligomers (Table 10) were obtained after the solution stage of the reaction because of the low reactivity of these diamines By optimizing the synthesis conditions, it is possible to form films Good films of 6FDA/TFPDA were made from the product of the 130°C and 150°C reactions, but the product of 22°C reaction did not form a film 6FDA/OFB gave almost the same results The anhydride structure is an important factor in forming good film Neither TFPDA/BTDA nor TFPDA/PMDA formed films Imidization conditions are also an important factor in forming good film They followed the chain extension reaction by FTIR on sequentially cured and cooled films of 6FDA/OFB

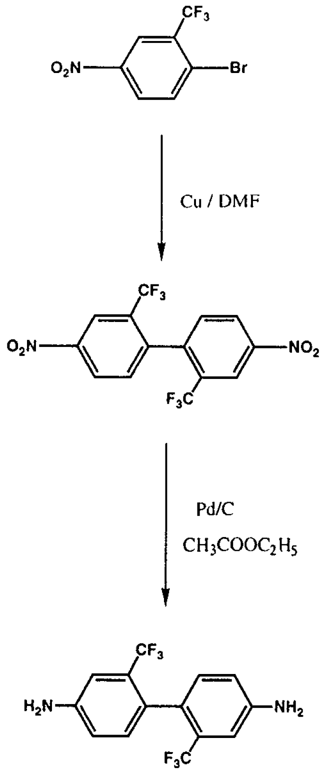
Table 7 Characteristics of Fluorinated Polyimides

Monomers		Imidization conditions	PAA viscosity[a]	Molecular	Film	Dielectric
Dianhydride	Diamine	Solvent, temperature(°C)/time(h)	(η[dl/g])	weight	formation	constant[b]
6FDA	PFDA	DMAc, 250 ~ 300/-	0 17	—	Yes	2 5
BTDA	PFDA	DMAc, 250 ~ 300/-	0 17	—	Yes	2 8
6FDA	4,4′-ODA	DMAc, 250 ~ 300/-	0 43	—	Yes	3 2
BTDA	4,4′-ODA	DMAc, 250 ~ 300/-	0 56	—	Yes	3 6

[a] Inherent viscosities were measured with 0 1 g/dl DMAc solution at 30°C

[b] Measurements were made at 10 kHz

Source Ref 14



TFDB

Figure 9 Synthesis route for TFDB (From Ref 15)

They found that the chain extension began at temperatures between 200°C and 300°C, but optimal mechanical properties were not obtained with curing temperatures below 350°C Figure 14 shows the synthesis scheme used to prepare 6FDA/OFB polyimide

At 100 kHz, the dielectric constant of the dry 6FDA/TFPDA was 2 75 and that of 6FDA/OFB was 2 75 The glass transition temperatures of both of these polyimides were above 330°C

Perfluoro aromatic diamines have poor reactivity, so it is necessary to optimize the reaction conditions in order to obtain good films on the polyimides prepared from perfluoro aromatic diamines

D. Fluorinated Polyimides Prepared from Benzotrifluoride-Based Diamines

Gerber et al [22] synthesized fluorinated polyimides from 3,5-diaminobenzotrifluoride (35-DABTF) and nine dianhydrides Figure 15 shows the chemical structures of the polyimides prepared from 35-DABTF, and their characteristics are shown in Table 11 Poly(amic acid)s

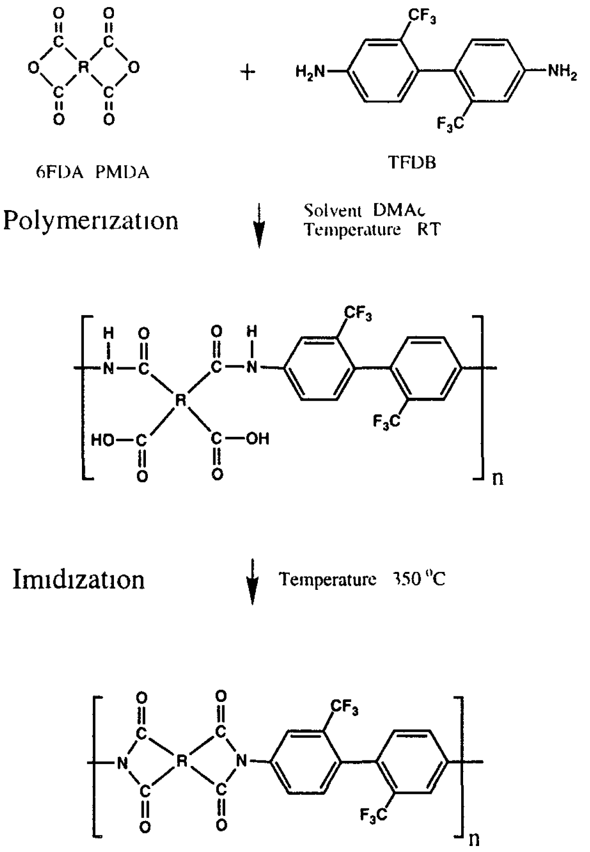


Figure 10 Synthesis scheme for fluorinated polyimides from TFDB (From Ref 16.)

prepared from 35-DABTF had relatively high intrinsic viscosities, from 0.3 to 0.9 dl/g, and they produced good films. Introducing a trifluoromethyl group into diamine did not affect the reactivity of the diamine. 35-DABTF/6FDA polyimide had the lowest dielectric constant, 2.58 at 10 GHz, among the nine polyimides prepared from 35-DABTF and had a relatively high glass transition temperature of almost 300°C.

Buchanan et al. [23] have synthesized fluorinated polyimides from CF_3-substituted oxydianiline 4,4′-oxy-bis[3(trifluoromethyl)benzenamine] (124-OBABTF), which was synthesized in two steps from 2-chloro-5-nitrobenzotrifluoride as described by Maki and Inukai [15]. Figure 16 shows the chemical structure of the fluorinated polyimides obtained from 124-OBABTF, and their characteristics are shown in Table 12. Five poly(amic acid)s were prepared in the conventional way. Their inherent viscosities were above 1.0 dl/g in most cases despite the presence of the strongly electron-withdrawing CF_3 groups of 124-OBABTF. Thermal imidization of the PAAs produced polyimide films that were tough, clear, and nearly colorless. The dielectric constants of these polyimides are of particular interest. The most highly fluorinated polyimide, 124-OBABTF/6FDA, had a dielectric constant of 2.76 at 1 MHz, and its glass transition temperature was 295°C.

Table 8 Characteristics of Fluorinated Polyimides

Monomers		Imidization conditions	PAA viscosity[a]	Molecular	Film	Dielectric
Dianhydride	Diamine	Solvent, temperature(°C)/time(h)	(η[dl/g])	weight	formation	constant[b]
PMDA	TFDB	DMAc, 70/2, 160/1, 200/0 5, 350/1 (N_2)	1 79	—	Yes	3 2
6FDA	TFDB	DMAc, 70/2, 160/1, 200/0 5, 350/1 (N_2)	1 00	—	Yes	2 8

[a] Inherent viscosities were measured with DMAc solution at 30°C
[b] Measurements were made at 23°C and 1 MHz under dry conditions
Source Ref 16

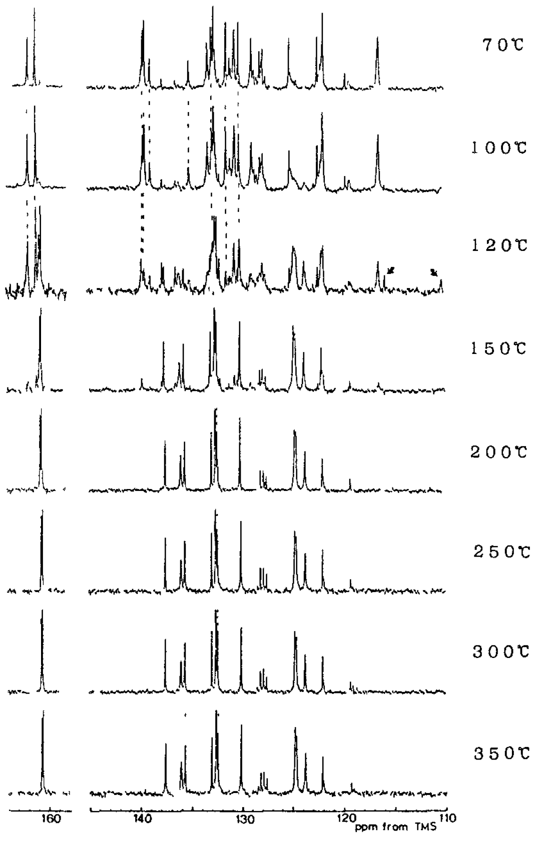


Figure 11 ^{13}C NMR proton-decoupled spectra of 6FDA/TFDB samples cured at various temperatures (From Ref 17)

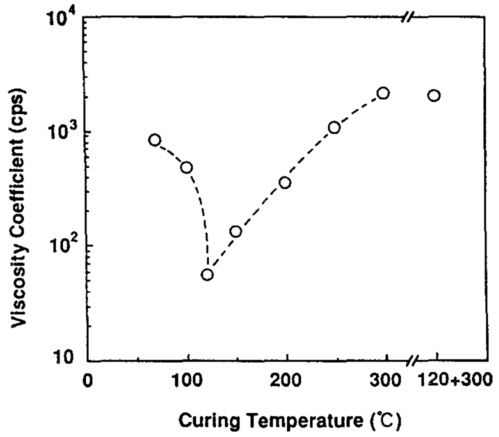


Figure 12 Viscosity coefficients of 15 wt% DMAc solutions of 6FDA/TFDB polyimide as a function of curing temperature (From Ref 17)

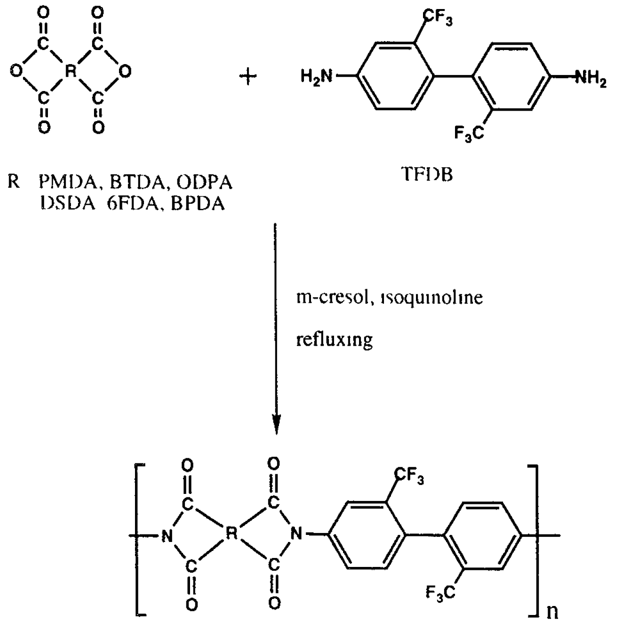


Figure 13 Synthesis scheme for the fluorinated polyimides from TFDB (From Ref 20)

Incorporation of benzotrifluoride moiety into polyimide is an effective way to lower the dielectric constant while maintaining the glass transition temperature

E. Fluorinated Polyimides Prepared from O-Substituted Diamines

Misra et al [24] have synthesized fluorinated polyimides from 6FDA and seven fluorinated diamines with varying structures in order to study the effect of different fluorinated segments upon the dielectric constant They synthesized the novel diamines 4FBDA, DTDE, DTHE, and TFATDFDADP [25] Figure 17 shows the synthesis scheme for the fluorinated polyimides, and their characteristics are shown in Table 13 After the room temperature reaction, the PAAs from BAT, BAO, and BDAF were highly viscous, whereas those from 4FBDAF, DTDE, DTHE, and TFATDFDADP showed no appreciable increase in solution viscosity After heating at 100°C, the solution viscosity of the poly(amic acid)s from 4FBDAF, DTHE, and TFATDFDADP increased Their number average molecular weights are given in Table 13 The molecular weight of 6FDA/DTDE was very low, those of 6FDA/BAT and 6FDA/DTHE were from 4000 to 9000, and those of 6FDA/TFATDFDADP, 6FDA/BAT, 6FDA/BAO, and 6FDA/BDAF were all above 15,000 Misra et al [24] concluded that these were due to decreased nucleophilic reactivity of the amine caused by the presence of a strong electron-withdrawing group *ortho* to the amino group (fluorine atoms in 4FBDAF, and fluorinated acryloxy or alkoxy groups in DTDE and DTHE) 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 with polyimide from diamine DTDE At 100 kHz, the dielectric constants of the polyimides prepared from diamines DTHE and TFATDFDADP were 2 93 The correlation between the dielectric constant and the fluorine content was weak because of the lack of systemic variation in the polymer structures The

Table 9 Characteristics of Fluorinated Polyimides

Monomers		Imidization conditions	PAA viscosity[a]	Molecular	Film	Dielectric
Dianhydride	Diamine	Solvent, temperature(°C)/time(h)	(η[dl/g])	weight	formation	constant[b]
PMDA	TFDB	Refluxing *m*-cresol (chemical)	—	—	Yes	—
BTDA	TFDB	Refluxing *m*-cresol (chemical)	1.6	—	Yes	—
ODPA	TFDB	Refluxing *m*-cresol (chemical)	1.1	—	Yes	—
DSDA	TFDB	Refluxing *m*-cresol (chemical)	1.0	—	Yes	—
6FDA	TFDB	Refluxing *m*-cresol (chemical)	1.9	—	Yes	—
BPDA	TFDB	Refluxing *m*-cresol (chemical)	4.9	—	Yes	2.5

[a] Inherent viscosities were measured with polyimide *m*-cresol solution at 30°C

[b] ASTM D-150

Source Ref 20

Table 10 Characteristics of Fluorinated Polyimides

Monomers		Imidization conditions	PAA viscosity	Molecular	Film	Dielectric
Dianhydride	Diamine	Solvent, temperature(°C)/time(h)	(η[dl/g])	weight[a]	formation	constant[b]
6FDA	TFPDA	NMP, room temp ~ 150, 350	—	940 ~ 1381	Yes	2 75
6FDA	PDA	NMP, room temp ~ 200, 350	—	—	Yes	2 9
6FDA	OFB	NMP, 50 ~ 200, 350	0 03–0 045	1480	Yes	2 75
PMDA	TFPDA	NMP, room temp ~ 200, 350	—	—	No	—
BPDA	TFPDA	NMP, 75 ~ 200, 350	—	714 ~ 890	No	—
BPDA	PDA	NMP, room temp ~ 200, 350	—	—	Yes	2 9
BTDA	TFPDA	NMP, room temp ~ 200, 350	—	—	No	—

[a] Number-average molecular weights by GPC of PAA in THF

[b] Measurements were made at 100 kHz under dry conditions

Source Ref 21

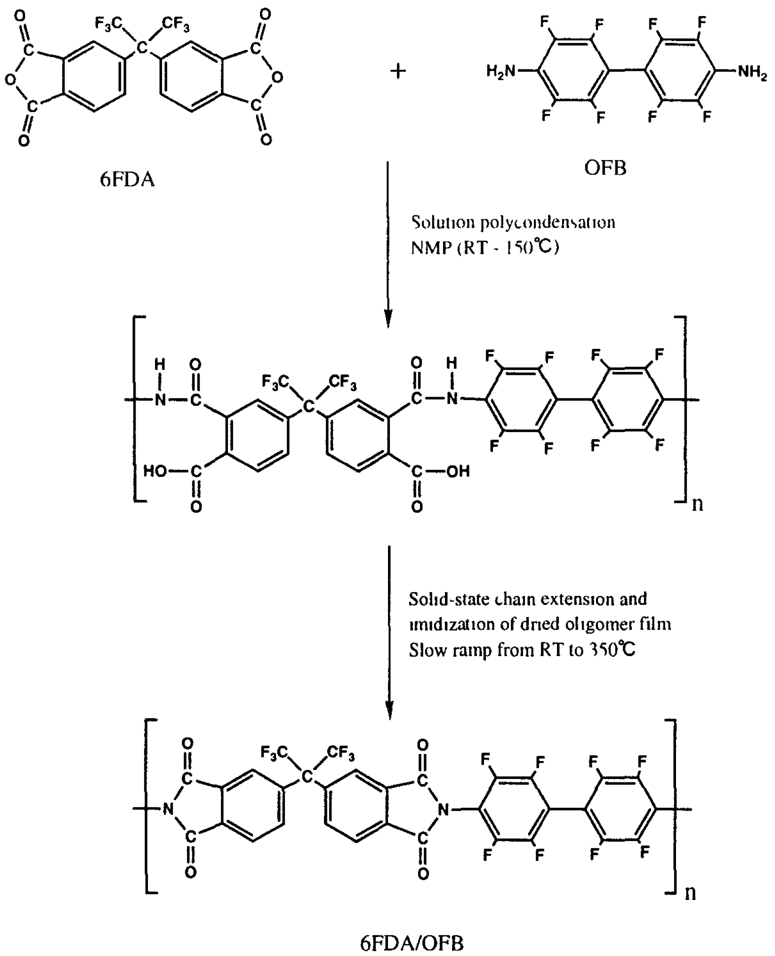
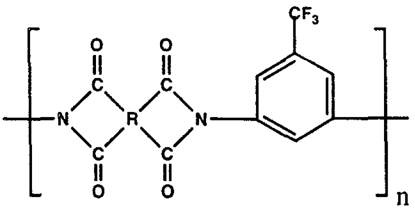


Figure 14 Synthesis scheme for 6FDA/OFB polyimide (From Ref 21)



R BTDA, 6FDA, ODPA, BPDA, IDPA,
PMDA, SiDA, DSDA, BTSDA

Figure 15 Chemical structure of the polyimides from 35-DABTF (From Ref 22)

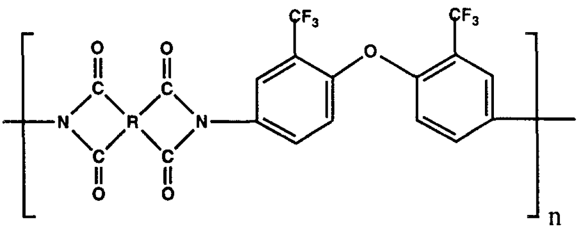
Table 11 Characteristics of Fluorinated Polyimides

Monomers		Imidization conditions	PAA viscosity[a]	Molecular	Film	Dielectric
Dianhydride	Diamine	Solvent, temperature(°C)/time(h)	(η[dl/g])	weight	formation	constant[b]
BTDA	35-DABTF	DMAc, 100/1, 200/2, 300/1 (air)	0 53	—	Yes	2 90
6FDA	35-DABTF	DMAc, 100/1, 200/2, 300/1 (air)	0 70	—	Yes	2 58
ODPA	35-DABTF	DMAc, 100/1, 200/2, 300/1 (air)	0 34	—	Yes	2 91
BPDA	35-DABTF	DMAc, 100/1, 200/2, 300/1 (air)	0 89	—	Yes	3 02
IPDA	35-DABTF	DMAc, 100/1, 200/2, 300/1 (air)	0 53	—	Yes	—
PMDA	35-DABTF	DMAc, 100/1, 200/2, 300/1 (air)	0 93	—	No	—
SiDA	35-DABTF	DMAc, 100/1, 200/2, 300/1 (air)	0 64	—	No	2 75
DSDA	35-DABTF	DMAc, 100/1, 200/2, 300/1 (air)	0 51	—	No	—
BTSDA	35-DABTF	DMAc, 100/1, 200/2, 300/1 (air)	0 37	—	Yes	—

[a] Inherent viscosities were measured with 0 5 wt% DMAc solution at 35°C

[b] Measurements were made at 10 GHz

Source Ref 22



R 6FDA, ODPA, BPDA,
PMDA, BTDA

Figure 16 Chemical structure of the polyimides from 124-OBABTF (From Ref 23)

results also suggest that at comparable fluorine contents, fluorine bound to an aromatic ring lowers the dielectric constant more than aliphatic fluorine does (compare, for example, the polyimides from BAT and BAO with that from BDAF)

F. Fluorinated Polyimides Prepared from (Mono- or Bis-trifluoromethyl)benzenetetracarboxylic Dianhydrides

This section describes a study of fluorinated polyimides with a rigid-rod structure. The main purpose of this study was to obtain a low dielectric constant and low thermal expansion

Matsuura et al [26] synthesized a series of new fluorinated rigid-rod polyimides by the reaction of TFDB with 1,4-bis(trifluoromethyl)-2,3,5,6-benzenetetracarboxylic dianhydride (P6FDA), 1-(trifluoromethyl)-2,3,5,6-benzenetetracarboxylic dianhydride (P3FDA), or PMDA Figure 18 shows the synthesis route for P6FDA

Figure 19 shows the synthesis scheme for the fluorinated rigid-rod polyimides prepared from P6FDA and TFDB Table 14 shows the characteristics of the fluorinated polyimides prepared from P6FDA and P3FDA. The intrinsic viscosities of P6FDA/TFDB, P3FDA/TFDB, and PMDA/TFDB poly(amic acid)s were 0 6, 0.7, and 1 8 dl/g, respectively, and these decreased with increasing number of trifluoromethyl side chains in the dianhydride unit Matsuura et al. [26] suggested two reasons for this behavior: it is easy to open the dianhydride ring by introducing trifluoromethyl group, and chain–chain interaction decreases with increasing fluorine content All the poly(amic acid)s produced good films The coefficients of thermal expansion of P6FDA/TFDB, P3FDA/TFDB, and PMDA/TFDB were -0 5 × 10^{-5} °C^{-1}, 2 8 × 10^{-5} °C^{-1}, and 5.6 × 10^{-5} °C^{-1}, respectively, and increased with the number of trifluoromethyl side chains in the dianhydride unit This shows that the trifluoromethyl side group loosened the molecular packing The dielectric constants at 1 MHz of PMDA/TFDB, P3FDA/TFDB, and P6FDA/TFDB were 3.2, 2 8, and 2 6, respectively, and decreased as the fluorine content increased.

This study showed that fluorinated polyimides with a rigid-rod structure can have both a low dielectric constant and low thermal expansion, and that the position of the trifluoromethyl groups is important for a low CTE.

Table 12 Characteristics of Fluorinated Polyimides

Monomers		Imidization conditions	PAA viscosity[a]	Molecular	Film	Dielectric
Dianhydride	Diamine	Solvent, temperature(°C)/time(h)	(η[dl/g])	weight	formation	constant[b]
ODPA	124-OBABTF	DMAc, 100/0 5, 200/0 5, 300/1 (air)	1 23	—	Yes	3 14
6FDA	124-OBABTF	DMAc, 100/0 5, 200/0 5, 300/1 (air)	0 60	—	Yes	2 76
BPDA	124-OBABTF	DMAc, 100/0 5, 200/0 5, 300/1 (air)	1 79	—	Yes	3 20
PMDA	124-OBABTF	DMAc, 100/0 5, 200/0 5, 300/1 (air)	1 25	—	Yes	3 16
BTDA	124-OBABTF	DMAc, 100/0 5, 200/0 5, 300/1 (air)	1 41	—	Yes	3 22

[a] Inherent viscosities were measured with 0 5 wt% DMAc solution at 35°C

[b] Measurements were made at 50% RH and 1 MHz

Source Ref 23

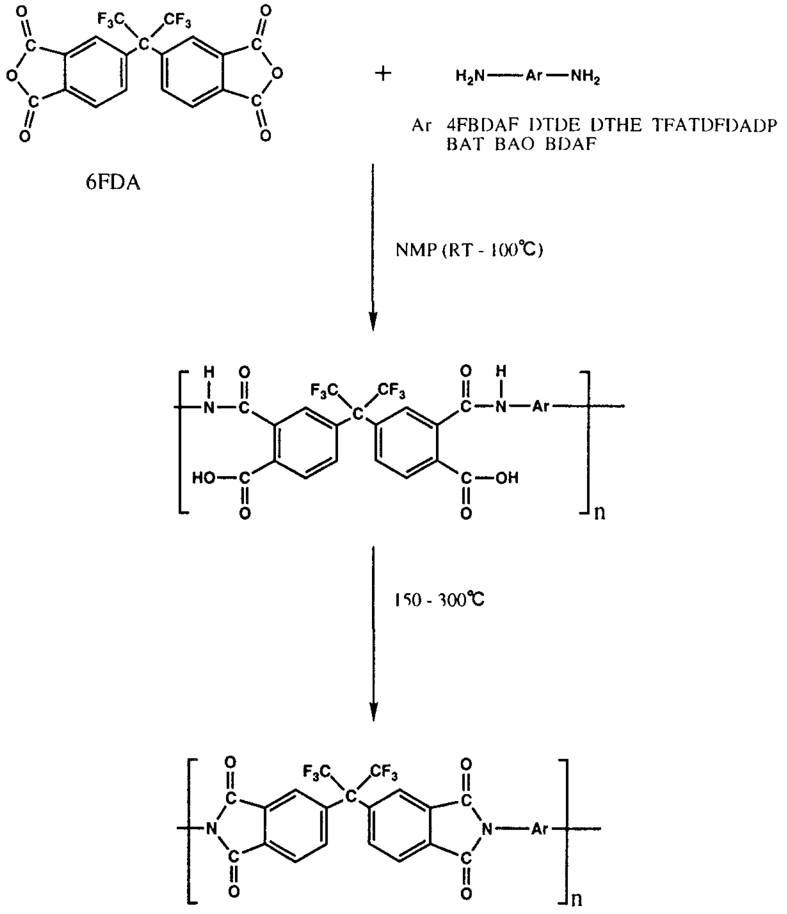


Figure 17 Synthesis scheme for the fluorinated polyimides (From Ref 24)

G. Fluorinated Polyimides Prepared from Rigid Fluorinated Dianhydrides

Trofimenko [27] synthesized a new class of rigid fluorinated monomers for polyimides based on a 9,9-disubstituted xanthene core The aim was to obtain polyimides with a high glass transition temperature, low coefficient of thermal expansion, low dielectric constant, and low water absorption all at the same time He synthesized two dianhydrides, 9,9-bistrifluoromethyl-2,3,6,7-xanthenetetracarboxylic dianhydride (6FCDA) and 9-phenyl-9-trifluoromethyl-2,3,6,7-xanthenetetracarboxylic dianhydride (3FCDA) Figure 20 shows the synthesis route for 6FCDA and 3FCDA

Auman [28] synthesized novel fluorinated polyimides from 6FCDA or 3FCDA and nine diamines including a rigid fluorinated diamine like TFDB. Figure 21 shows the synthesis scheme for the fluorinated polyimides from 6FCDA or 3FCDA, and their characteristics are shown in Table 15 He used two methods to synthesize the polyimides synthesis of the poly-

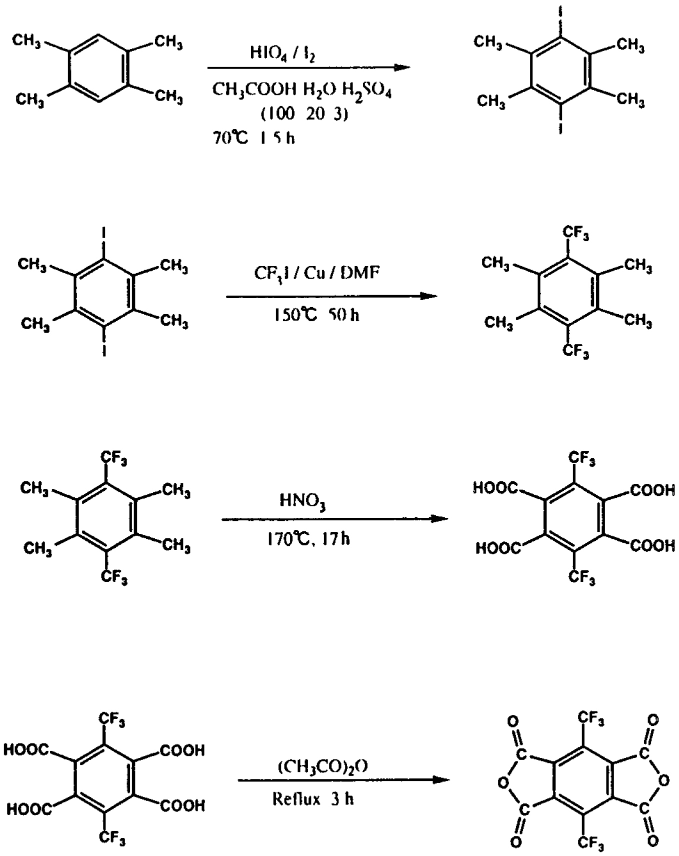
Table 13 Characteristics of Fluorinated Polyimides

Monomers		Imidization conditions.	PAA viscosity	Molecular	Film	Dielectric
Dianhydride	Diamine	Solvent, temperature(°C)/time(h)	(η[dl/g])	(M_w) weight[a]	formation	constant[b]
6FDA	4FBDAF	NMP, 70/12, 100/2, 150/2,200/2,250/2,300/1	—	3964	No	—
6FDA	DTDE	NMP, 70/12, 100/2, 150/2,200/2,250/2,300/1	—	417	No	—
6FDA	DTHE	NMP, 70/12, 100/2, 150/2,200/2,250/2,300/1	—	8507	Yes	2.93
6FDA	TFATFDFDADP	NMP, 70/12, 100/2, 150/2,200/2,250/2,300/1	—	29,297	Yes	3.00
6FDA	BAT	NMP, 70/12, 100/2, 150/2,200/2,250/2,300/1	—	15,602	Yes	2.95
6FDA	BAO	NMP, 70/12, 100/2, 150/2,200/2,250/2,300/1	—	30,402	Yes	2.95
6FDA	BDAF	NMP, 70/12, 100/2, 150/2,200/2,250/2,300/1	—	27,600	Yes	2.99

[a] Number-average molecular weights by GPC of PAA in THF

[b] Measurements were made at 22°C, 50% RH and 100 kHz

Source Ref 24



P6FDA

Figure 18 Synthesis route for P6FDA (From Ref 26)

(amic acid) with subsequent coating and thermal curing, and direct synthesis of the polyimide in one pot by solution imidization in an NMP/N-cyclohexylpyrollidinone (CHP) solvent mixture at 180–190°C.

He found that combining rigid fluorinating dianhydrides with a rodlike fluorinated diamine like TFDB produced polyimide films with an ideal combination of low dielectric constant, low moisture absorption, and low CTE. The polyimide from 6FCDA and TFDB had a low dielectric constant of 2 4 at 1 MHz, low CTE of 6 ppm, low moisture absorption of 1 2 wt% at 85% relative humidity (RH), and high glass transition temperature of 420°C

The fluorinated polyimides from 6FCDA or 3FCDA and a rigid fluorinated diamine are very attractive for electronics application

Auman and Trofimenko [29] have reported the synthesis of fluorinated, high glass transition temperature, soluble polyimides based on 12,14-diphenyl-12,14-bis(trifluoromethyl)-12H,14H-5,7-dioxapentacene-2,3,9,10-tetracarboxylic dianhydride (PXPXDA). The chemical structure of the fluorinated polyimides is shown in Figure 22, and their characteristics are shown

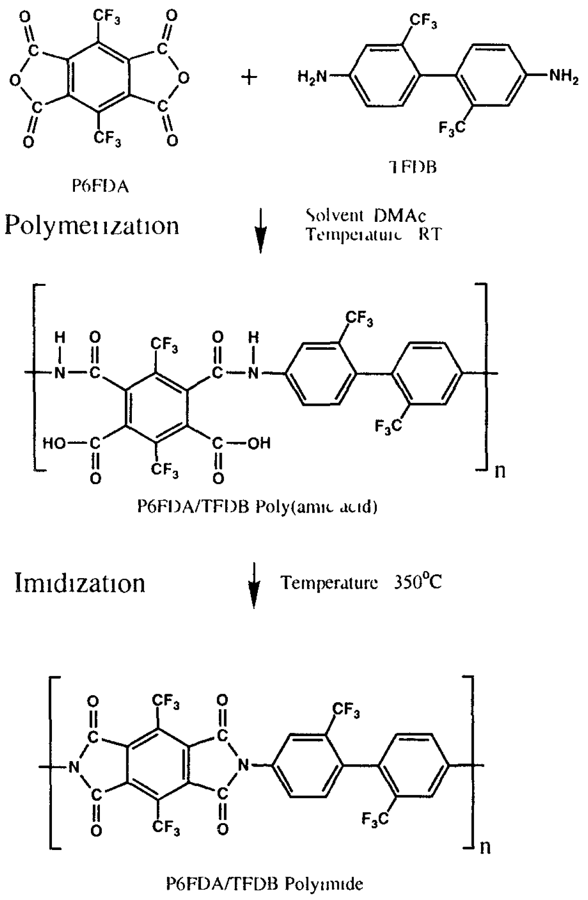


Figure 19 Synthesis scheme for the fluorinated polyimides from P6FDA and TFDB (From Ref 26)

in Table 16 The polyimide synthesis was carried out in the same two ways, as for 6FCDA and 3FCDA The molecular weights of the PAAs and polyimides were all high PXPXDA/TFDB had a low dielectric constant of 2 6 at 1 MHz and low CTE of 10 ppm

H. Fluorinated Polyimides Prepared from 2,2′-Bis(fluoroalkoxy)benzidines

The previous section showed that TFDB is suitable as a diamine for fluorinated, rigid-rod polyimide Feiring et al [30] have investigated the synthesis and properties of fluorinated polyimides prepared from novel 2,2′-bis(fluoroalkoxy)benzidines. Figure 23 shows the synthesis scheme for the polyimides from 2,2′-bis(fluoroalkyoxy)benzidines, and their characteristics are shown in Table 17. The three new diamines were synthesized from the corresponding 3-(fluoroalkyoxy)nitrobenzenes by reduction, followed by benzidine rearrangement The fluorinated polyimides from the three diamines (TFMOB, TFEOB, DFPOB) were synthesized

Table 14 Characteristics of Fluorinated Polyimides

Monomers						
Dianhydride	Diamine	Imidization conditions Solvent, temperature(°C)/time(h)	PAA viscosity[a] (η[dl/g])	Molecular weight	Film Yes/No formation	Dielectric constant[b]
PMDA	TFDB	DMAc, 70/2, 160/1, 200/0.5, 350/1 (N_2)	1.8	—	Yes	3.2
P3FDA	TFDB	DMAc, 70/2, 160/1, 200/0.5, 350/1 (N_2)	0.7	—	Yes	2.8
P6FDA	TFDB	DMAc, 70/2, 160/1, 200/0.5, 350/1 (N_2)	0.6	—	Yes	2.6
PMDA	DMDB	DMAc, 70/2, 160/1, 200/0.5, 350/1 (N_2)	2.7	—	Yes	—
P3FDA	DMDB	DMAc, 70/2, 160/1, 200/0.5, 350/1 (N_2)	1.3	—	Yes	—
P6FDA	DMDB	DMAc, 70/2, 160/1, 200/0.5, 350/1 (N_2)	0.7	—	Yes	—
PMDA	DPTP	DMAc, 70/2, 160/1, 200/0.5, 350/1 (N_2)	1.3	—	Yes	—
P3FDA	DPTP	DMAc, 70/2, 160/1, 200/0.5, 350/1 (N_2)	0.3	—	Yes	—
P6FDA	DPTP	DMAc, 70/2, 160/1, 200/0.5, 350/1 (N_2)	0.2	—	Yes	—

[a] Inherent viscosities were measured with DMAc solution at 30°C

[b] Measurements were made at 23°C and 1 MHz under dry conditions

Source Ref 26

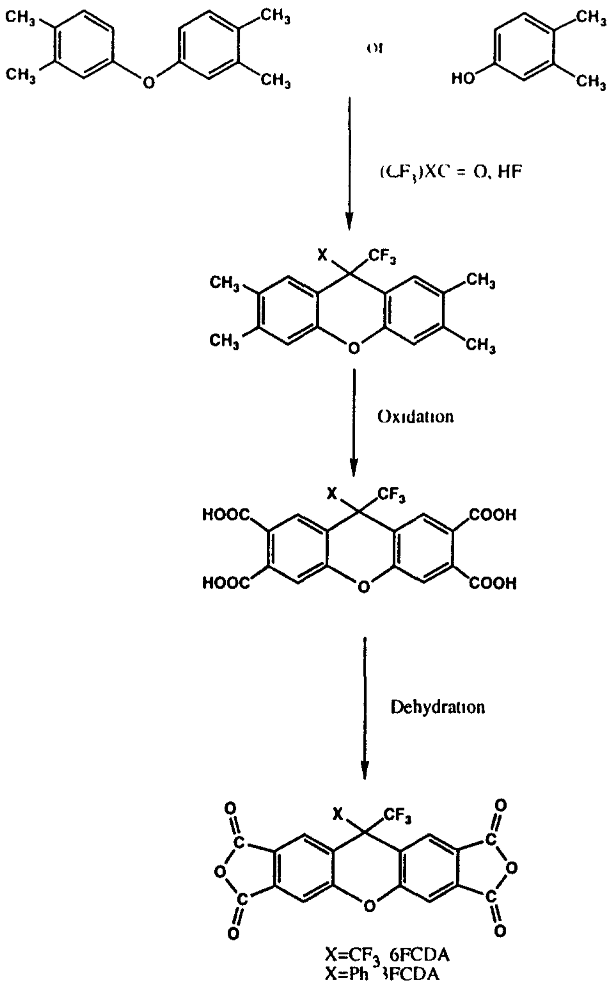


Figure 20 Synthesis route for 6FCDA and 3FCDA (From Ref 27)

using the conventional polymerization and one-pot solution polymerization. The polyimides had high molecular weights and gave good films. Trifluoromethoxy substitution was shown to give properties similar to trifluoromethyl substitution. The polyimide from 6FCDA and TFMOB had a low dielectric constant of 2 8 at 1 MHz, low CTE of 10 ppm, low moisture absorption of 0 8 wt% at 85% RH, and high glass transition temperature of 375°C.

I. Fluorinated Polyimides Prepared from a Diamine Based on Trifluoroacetophenone

Rogers et al. [31] have synthesized very high glass transition temperature, soluble polyimides from a diamine based on trifluoroacetophenone. 1,1-bis(4-aminophenyl)-1-phenyl-2,2,2-trifluoroethane (3Fdiamine) was prepared using the procedure of Kray and Rosser [32] as shown in Figure 24. Figure 25 shows the synthesis scheme for the polyimides prepared from PMDA, 3Fdiamine, and phthalic anhydride Their characteristics are shown in Table 18.

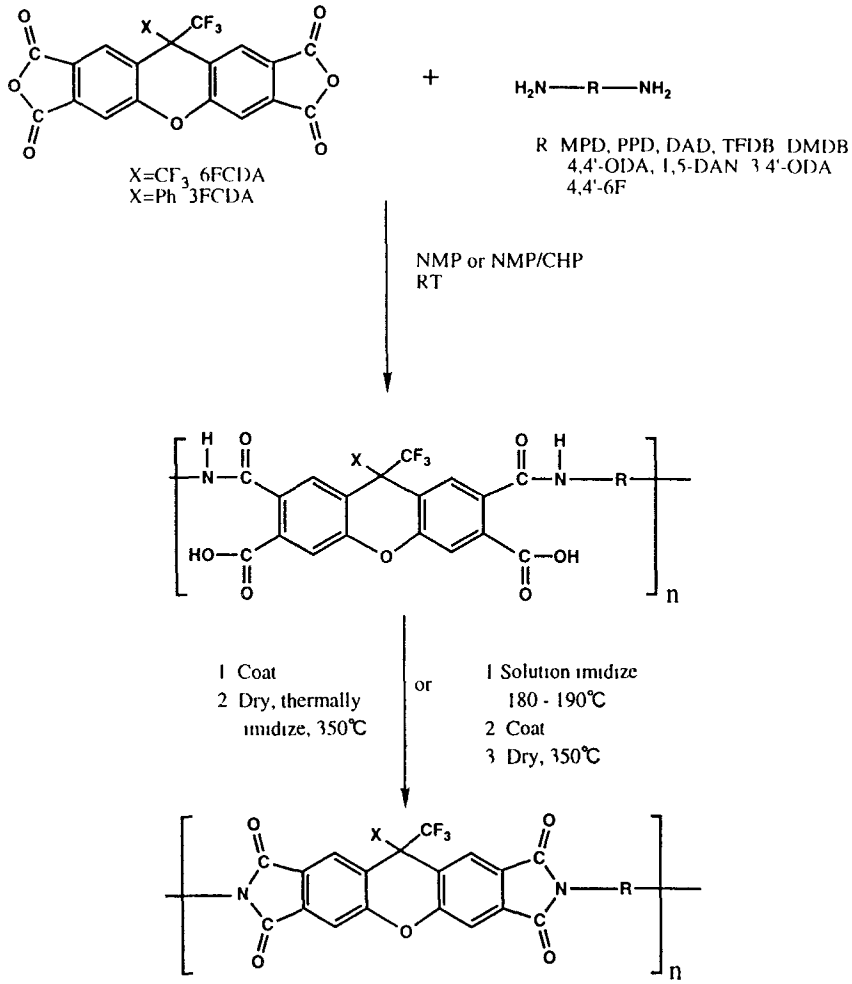


Figure 21 Synthesis scheme for the fluorinated polyimides from 6FCDA or 3FCDA. (From Ref. 28.)

A calculated amount of phthalic anhydride was added to the prepared diamine solution to afford nonreactive end groups and controlled molecular weights. The intrinsic viscosities of the three polyimides from PMDA, 6FDA, and BPDA were 0.65, 0.36, and 0.47 dl/g, respectively. These polyimides were soluble in NMP, and tough films could be formed from the polyimide solutions. The PMDA/3Fdiamine polyimide exhibited a glass transition temperature exceeding 420°C.

Soluble polyimides with high glass transition temperature could be synthesized from 3Fdiamine.

III. FLUORINATED POLYIMIDES FOR OPTO-ELECTRONICS

Optical polymers are expected to be used for optical communications. Such optical polymers require thermal stability above 300°C as well as good transparency because they must be

Table 15 Characteristics of Fluorinated Polyimides

Monomers		Imidization conditions	PAA viscosity	Molecular	Film	Dielectric
Dianhydride	Diamine	Solvent, temperature(°C)/time(h)	(η[dl/g])	weight	formation	constant[d]
6FCDA	4,4′-ODA	NMP, 350/–	—	250,000[a]	Yes	2 8
6FCDA	3,4′-ODA	NMP, 350/–	—	207,000[a]	Yes	2 9
6FCDA	MPD	NMP, 350/–	—	147,000[a]	Yes	—
6FCDA	PPD	NMP, 350/–	—	117,000[a]	Yes	—
6FCDA	4,4′-6F	NMP, 350/–	—	143,000[a]	Yes	—
6FCDA	DAD	NMP, 350/–	—	203,000[a]	Yes	—
6FCDA	TFDB	NMP, 350/–	—	215,000[a]	Yes	—
6FCDA	DMDB	NMP, 350/–	—	251,000[a]	Yes	—
3FCDA	4,4′-ODA	NMP, 350/–	—	325,000[a]	Yes	—
3FCDA	3,4′-ODA	NMP, 350/–	—	241,000[a]	Yes	—
3FCDA	MPD	NMP, 350/–	—	229,000[a]	Yes	—
3FCDA	PPD	NMP, 350/–	—	266,000[a]	Yes	—
3FCDA	4,4′-6F	NMP, 350/–	—	277,000[a]	Yes	—
3FCDA	DAD	NMP, 350/–	—	387,000[a]	Yes	—
3FCDA	1,5-DAN	NMP, 350/–	—	177,000[a]	Yes	—
3FCDA	TFDB	NMP, 350/–	—	396,000[a]	Yes	—
3FCDA	DMDB	NMP, 350/–	—	298,000[a]	Yes	—
6FCDA	4,4′6F	NMP/CHP, 180–190 (chemical)	—	102,000[b]	Yes	2 3
3FCDA	4,4′-ODA	NMP/CHP, 180–190 (chemical)	—	327,000[c]	Yes	2 8
3FCDA	3,4′-ODA	NMP/CHP, 180–190 (chemical)	—	167,000[c]	Yes	2 8
3FCDA	MPD	NMP/CHP, 180–190 (chemical)	—	204,000[c]	Yes	2 7
3FCDA	4,4′-6F	NMP/CHP, 180–190 (chemical)	—	321,000[c]	Yes	2 5
3FCDA	DAD	NMP/CHP, 180–190 (chemical)	—	228,000[b]	Yes	—

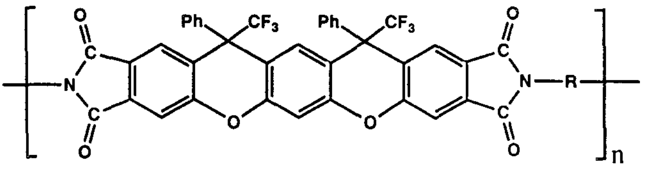
[a] Number-average molecular weights by GPC of PAA in DMAc/LiBr/H_3PO_4/THF at 35°C

[b] Number-average molecular weights by GPC of polyimide in DMAc at 135°C

[c] Number-average molecular weights by GPC of polyimide in DMAc/LiBr/H_cPO_r/THF at 35°C

[d] Measurements were made at 0% RH and 1 MHz

Source Ref 28



R ODA, PPD, DAD, TFDB

Figure 22 Chemical structure of the polyimides from PXPXDA (From Ref 29)

compatible with conventional integrated circuit (IC) fabrication. As a consequence, conventional optical polymers, such as poly(methyl methacrylate) and polycarbonate, cannot be used in these applications because of their poor thermal stability

On the other hand, conventional polyimides like Kapton are reddish-brown in color and have not been used in optoelectronics applications Some fluorinated polyimides are transparent, so they look very promising as optical polymers In this section we first discuss an evaluation of fluorinated polyimides with a hexafluoroisopropylidene group as an optical waveguide material, and then discuss the synthesis and properties of several new fluorinated polyimides for optoelectronics

A. Fluorinated Polyimides with Hexafluoroisopropylidene Groups as an Optical Waveguide Material

Reuter et al [33] investigated the optical properties of three fluorinated polyimides from 6FDA These polyimides are all advertised as having good optical properties a Pyralin product (Du Pont) prepared from 6FDA and ODA, SiXEF-44 (American Hoechest) prepared from 6FDA and 4,4-6F, and SIXEF-33 (American Hoechest) prepared from 6FDA and 3,3-6F Figure 26 shows the chemical structures of the polyimides In their experiment, planar waveguides were produced by spin casting films onto glass substrates, and the optical losses were measured using a 633-nm He-Ne laser. The relationship between optical loss and curing conditions was investigated.

They found that the introduction of a hexafluoroisopropylidene group into the polyimide unit greatly improved the optical transparency of polyimides The optical losses ranged from very high for PMDA/ODA polyimide film through moderate for 6FDA/ODA polyimide film to low for 6FDA/4,4-6F polyimide film and 6FDA/3,3-6F polyimide film The 6FDA/4,4-6F polyimide film, after drying for 1 h at 90°C, has optical losses below 0 1 dB/cm at 633 nm. The low loss below 0 5 dB/cm ws retained at temperatures up to 200°C but the loss increased to more than 2 5 dB/cm with heating to 300°C They pointed out two possible causes for the observed waveguide losses. ordering with or without charge transfer complex formation, and voids or pinholes.

For waveguide application it is important to know the optical losses of typical fluorinated polyimides. The values are 0 5 dB/cm after 200°C annealing and 2 5 dB/cm after 300°C annealing

Table 16 Characteristics of Fluorinated Polyimides

Monomers		Imidization conditions	PAA viscosity	Molecular	Film	Dielectric
Dianhydride	Diamine	Solvent, temperature(°C)/time(h)	(η[dl/g])	weight	formation	constant[d]
PXPXDA	4,4′-ODA	NMP/CHP, 180–190 (chemical)	—	44,000[a], 68,400[b]	Yes	2 8
PXPXDA	PPD	NMP/CHP, 180–190 (chemical)	—	53,600[a]	No	—
PXPXDA	DAD	NMP/CHP, 180–190 (chemical)	—	38,100[c]	Yes	2 5
PXPXDA	TFDB	NMP/CHP, 180–190 (chemical)	—	68,400[b]	Yes	2 6

[a] Number-average molecular weights by GPC of polyimide in DMAc at 135°C

[b] Number-average molecular weights by GPC of polyimide in DMAc/LiBr/H_3PO_4/THF at 35°C

[c] Number-average molecular weights by GPC of PAA in DMAc/LiBr/H_3PO_4/THF at 35°C

[d] Measurements were made at 0% RH and 1 MHz

Source Ref 29

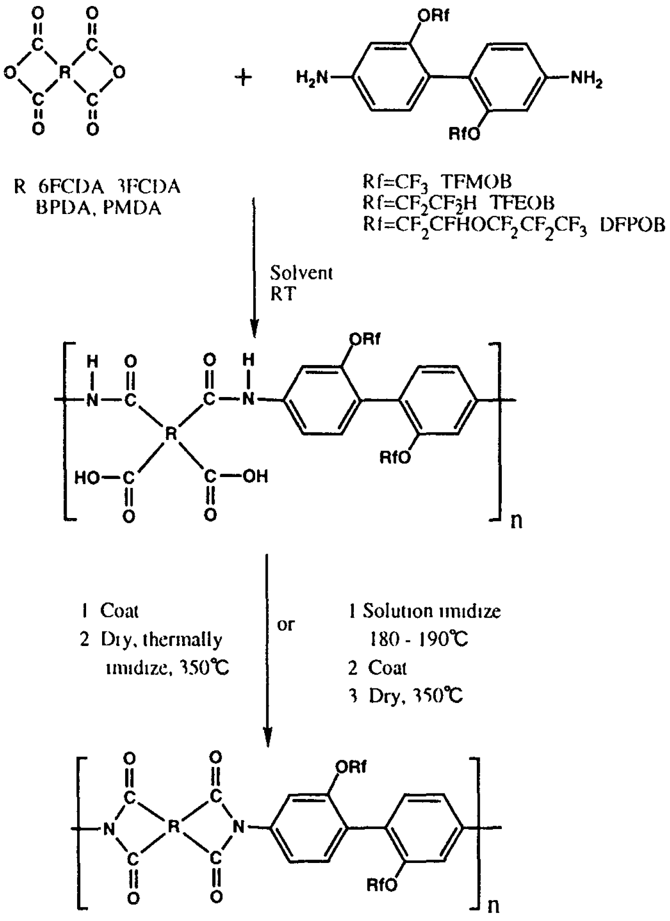


Figure 23 Synthesis scheme for the polyimides from 2,2′-bis(fluoroalkoxy)benzidines. (From Ref. 30.)

B. Fluorinated Polyimides from Bis(trifluoromethyl)diaminobiphenyl as an Optical Material

In Sec. II.B we saw that the fluorinated polyimide prepared from 6FDA and TFDB has high transparency, so it is expected to be useful as an optical material. The optical loss of 6FDA/TFDB polyimide film after high-temperature curing (350°C) was 0.7 dB/cm at the wavelength of 633 nm [34]. This value is much lower than that for 6FDA/4,4-6F polyimide films after 300°C curing (see Sec. III.A). Optical materials must have a controllable refractive index as well as being transparent. Matsuura et al. [35] have synthesized polyimide copolymers from 6FDA, PMDA, and TFDB in order to control the refractive index. Figure 27 shows the synthesis scheme for the copolyimides from 6FDA, PMDA, and TFDB. The refractive index at the wavelength of 589.3 nm of 6FDA/TFDB was 1.556, and that of PMDA/TFDB was 1.647. Thus, the refractive index can be controlled between 1.556 and 1.647 by the copolymerization of 6FDA, PMDA, and TFDB (Figure 28) [36].

Table 17 Characteristics of Fluorinated Polyimides

Monomers		Imidization conditions	PAA viscosity	Molecular	Film	Dielectric
Dianhydride	Diamine	Solvent, temperature(°C)/time(h)	(η[dl/g])	weight[a]	formation	constant[b]
6FCDA	TFDB	NMP/CHP, 180–190 (chemical)	—	126,000	Yes	2.4
6FCDA	TFMOB	NMP/CHP, 180–190 (chemical)	—	107,000	Yes	2.8
6FCDA	TFEOB	NMP/CHP, 180–190 (chemical)	—	88,800	Yes	3.0
6FCDA	DFPOB	NMP/CHP, 180–190 (chemical)	—	52,900	Yes	2.5
3FCDA	TFDB	NMP/CHP, 180–190 (chemical)	—	208,000	Yes	2.7
3FCDA	TFMOB	NMP/CHP, 180–190 (chemical)	—	149,000	Yes	2.6
3FCDA	TFEOB	NMP/CHP, 180–190 (chemical)	—	98,200	Yes	3.1
BPDA	TFDB	NMP/CHP, 180–190 (chemical)	—	315,000	Yes	2.9
BPDA	TFMOB	NMP/CHP, 180–190 (chemical)	—	165,000	Yes	2.7
BPDA	TFEOB	NMP/CHP, 180–190 (chemical)	—	113,000	Yes	3.3
BPDA	DFPOB	NMP/CHP, 180–190 (chemical)	—	65,900	Yes	2.7
PMDA	TFDB	NMP/CHP, 180–190 (chemical)	—	107,000	Yes	2.6
PMDA	TFMOB	NMP/CHP, 180–190 (chemical)	—	87,400	Yes	2.6
PMDA	TFEOB	NMP/CHP, 180–190 (chemical)	—	121,000	Yes	3.3
PMDA	DFPOB	NMP/CHP, 180–190 (chemical)	—	61,300	Yes	2.5

[a] Number-average molecular weights by GPC of polyimide in DMAc at 135°C

[b] Measurements were made at 0% RH and 1 MHz

Source Ref 30

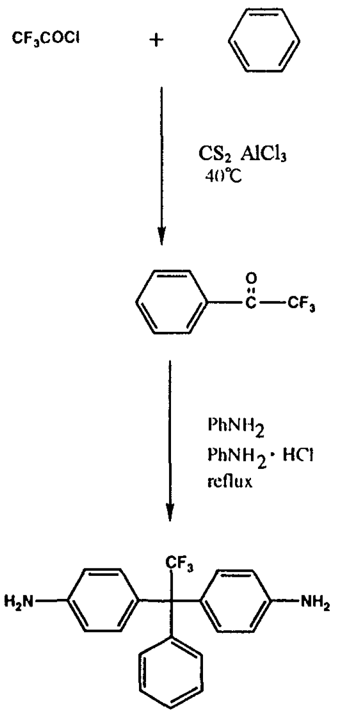


Figure 24 Synthesis route for 3Fdiamine (From Ref 32)

These polyimides had good transparency in the near-infrared region as well as in the visible region. Matsuura et al [37] fabricated optical ridge waveguides for optical communication components from these copolyimides, and at the wavelength of 1 3 µm, the optical loss of these waveguides was 0 3 dB/cm These polyimides waveguides have been used in optoelectronic multichip modules [38,39] In addition, single-mode optical waveguides made from these fluorinated polyimides were recently fabricated [40]

Besides waveguides, several other optical components such as optical filters [41] and optical waveplates [42] have been fabricated using optical polyimides made from 6FDA, PMDA, and TFDB.

C. Perfluorinated Polyimides

Although the fluorinated polyimides from 6FDA,PMDA, and TFDB have excellent properties as optical materials, there are some absorption peaks in the near-infrared region due to the harmonics of the carbon-hydrogen bonds [34] For optical communication use, Ando et al [43,44] proposed perfluorinated polyimides, in which fluorine-carbon bonds were substituted for hydrogen-carbon bonds, because these should have no absorption peaks between 1 0 and 1.7 µm They first investigated the synthesis of the perfluorinated polyimides using P6FDA, which is the only dianhydride without carbon-hydrogen bonds, and five perfluoro diamines

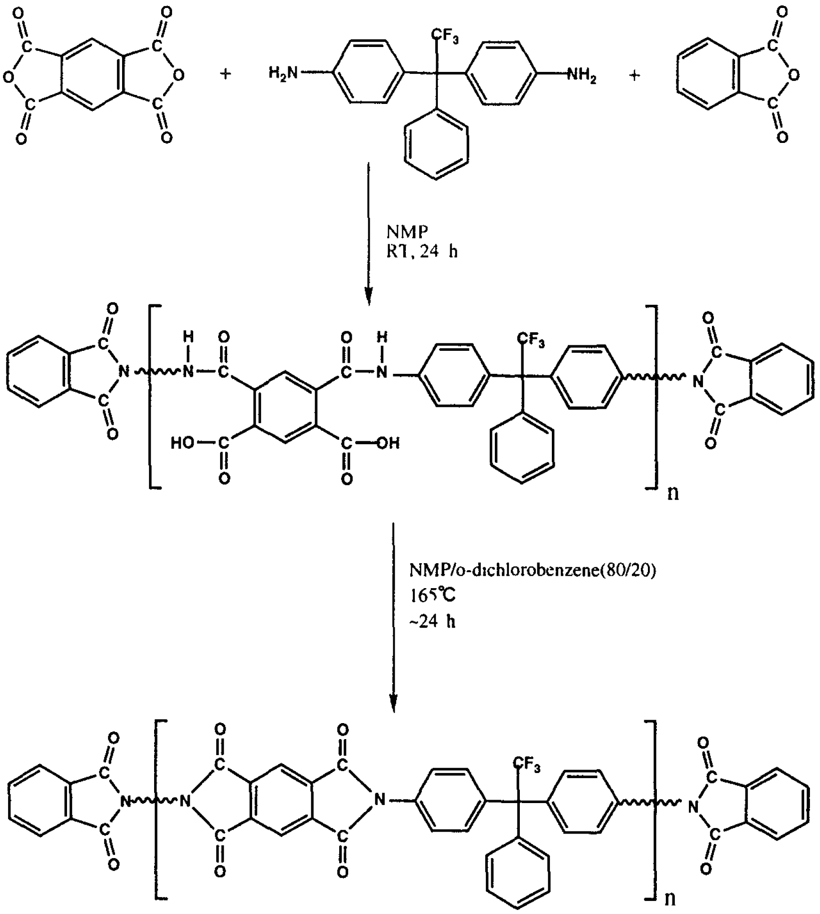


Figure 25 Synthesis scheme for the polyimides from 3Fdiamine (From Ref 26)

(Fig 29) The conventional two-step reaction was unable to produce a continuous film of perfluorinated polyimide

The primary reason for getting noncontinuous film was thought to be the poor reactivity of perfluoro diamines and the high rigidity of the polymer chain Therefore, they next synthesized a novel perfluorinated dianhydride with a flexible ether linkage, 1,4-bis(3,4-dicarboxytrifluorophenoxy) tetrafluorobenzene dianhydride (10FEDA), via a three-step reaction (Fig 30) An estimation of the reactivity of the five perfluorinated diamines by the reaction with phthalic anhydride, and ^{15}N and ^{1}H NMR study showed that tetrafluoro-m-phenylenediamine (4FMPD) was the most reactive among the five diamines [44]. Perfluorinated polyimide was synthesized from 10FEDA and 4FMPD, and a flexible film was formed (Fig 31) The perfluorinated polyimide had a high glass transition temperature (301 °C), and high initial polymer decomposition temperature (407 °C) The 10FEDA/4FMPD polyimide film cured at 200 °C was soluble in polar organic solvents Then, using the 10FEDA/4FMPD polyimide dissolved in acetone-d_6, the visible-near-infrared absorption spectrum was measured (Fig 32). The solid

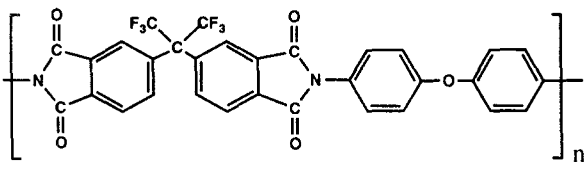
Table 18 Characteristics of fluorinated polyimides

Monomers		Imidization conditions	PI viscosity[a]	Molecular	Film	Dielectric
Dianhydride	Diamine	Solvent, temperature(°C)/time(h)	(η[dl/g])	weight	formation	constant
PMDA	3Fdiamine	NMP/DCB, 165 (chemical)	0 65	—	Yes	—
BPDA	3Fdiamine	NMP/DCB, 165 (chemical)	0 47	—	Yes	—
6FDA	3Fdiamine	NMP/DCB, 165 (chemical)	0 36	—	Yes	—

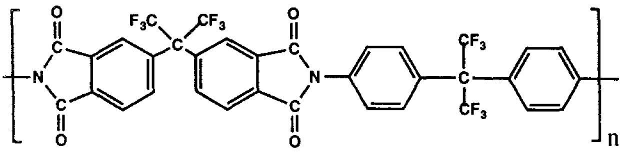
[a] Inherent viscosities were measured with NMP solution at 25°C

DCB, *o*-dichlorobenzene

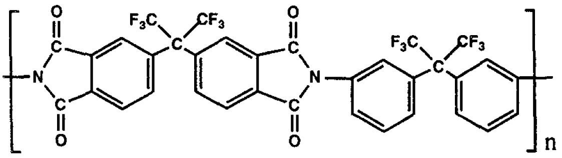
Source Ref 31



6FDA/ODA



6FDA/4,4-6F



6FDA/3,3-6F

Figure 26 Chemical structures of the fluorinated polyimides as an optical waveguide material. (From Ref. 33.)

line indicates the absorbance of 10FEDA/4FMPD and the dashed line indicates that of partially fluorinated polyimide (6FDA/TFDB). Except for a small absorption peak (at 1.4 μm) due to moisture, the perfluorinated polyimide has no substantial absorption peak over the wide wavelength range from 1.0 μm to 1.65 [44].

Perfluorinated polyimide with high transparency at the wavelengths of optical communications, 1.0–1.7 μm, is a promising material for optical communication applications.

IV. SUMMARY

Fluorinated polyimides have been extensively investigated mainly for electronics use. Since their first synthesis by Critchley et al. in 1972, many new fluorinated polyimides have been reported. If the fluorinated polyimides from 6FDA are considered the first-generation fluorinated polyimide, the ones currently being developed should be called second-generation fluorinated polyimides. These fluorinated polyimides for electronics use require several properties, such as low dielectric constant, low thermal expansion coefficient, and high glass transition

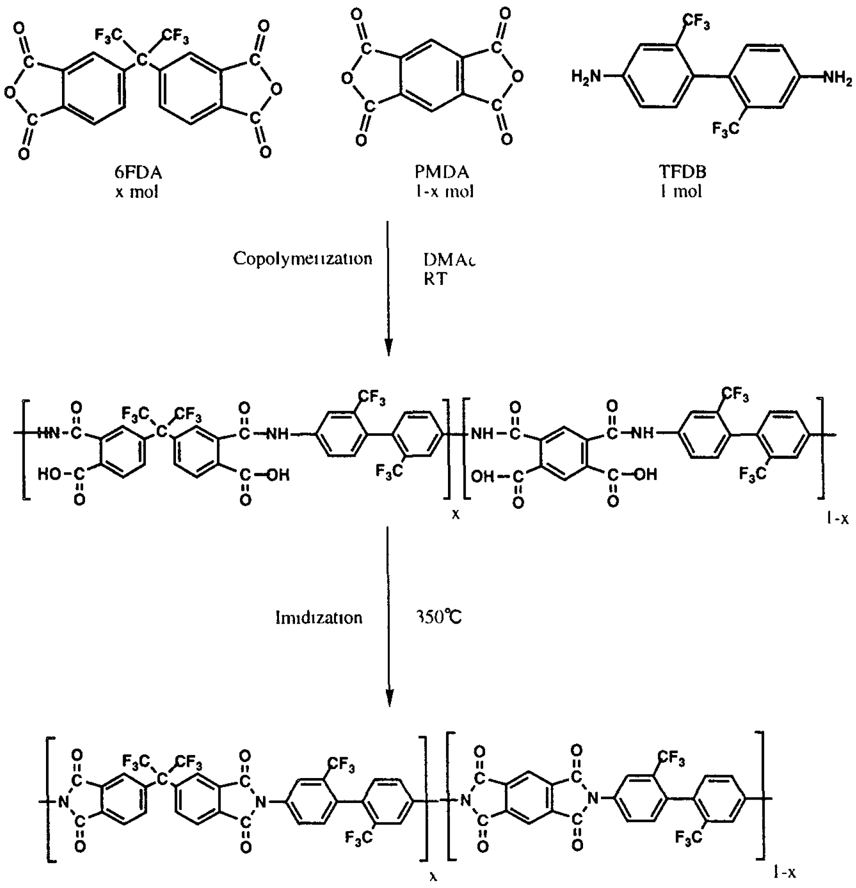


Figure 27 Synthesis scheme for the copolyimides from 6FDA, PMDA, and TFDB (From Ref 35)

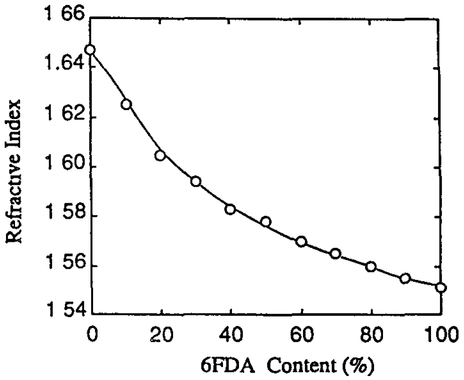
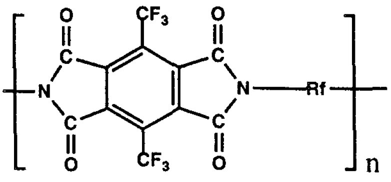


Figure 28 Refractive index of copolyimides from 6FDA, PMDA, and TFDB as a function of 6FDA content (From Ref 36)

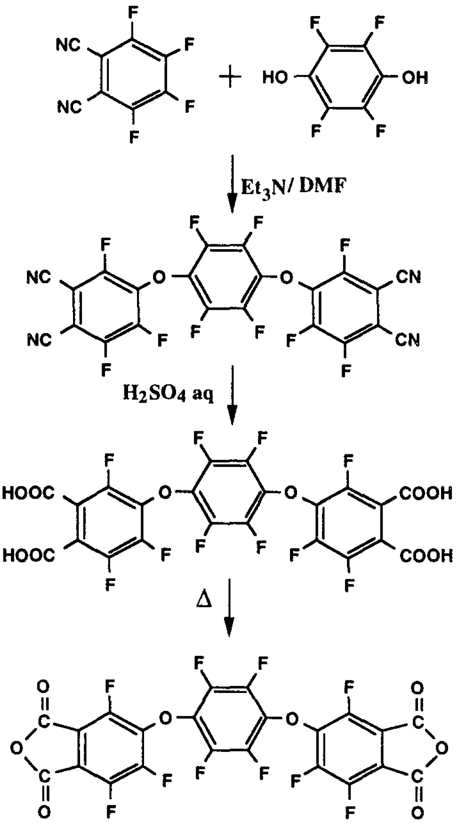


Rf TFPDA, OFB, 4FMPD, 8FODA, 8FSDA

Figure 29 Structure of perfluorinated polyimides from P6FDA (From Ref 43)

temperature, all at the same time. Investigations of fluorinated polyimides for optoelectronics use have also started recently These can be called the third-generation fluorinated polyimides.

A few difficult problems still pose challenge to the synthesis of the fluorinated polyimides. The main problem is the low reactivity of diamines caused by the introduction of a fluorinated substitute, which has a strong electron-attracting force and causes a steric effect. To solve this problem, one must select a fluorinated diamine that has high nucleophilic reactivity or find a new method of synthesizing fluorinated polyimide from a low-reactivity diamine. It is also



10FEDA

Figure 30 Synthesis route for 10FEDA (From Ref 43)

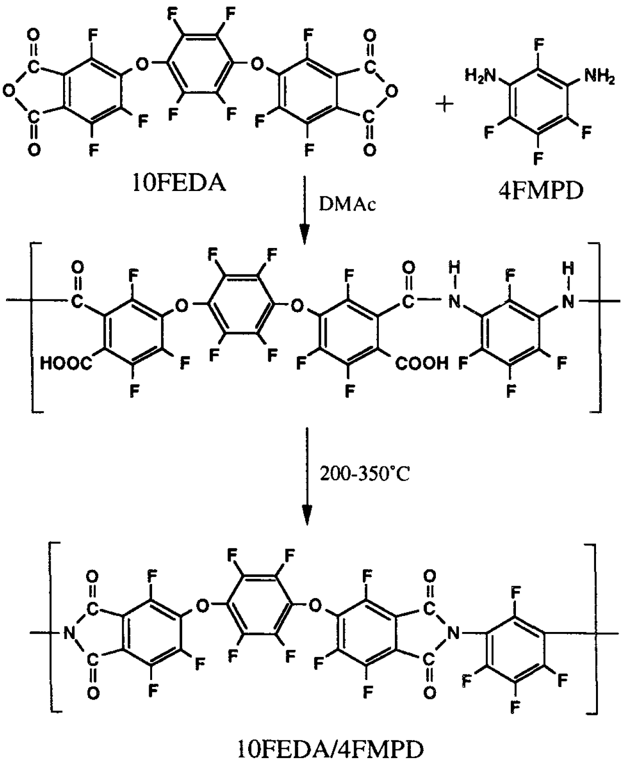


Figure 31 Synthesis scheme for perfluorinated polyimide from 10FEDA and 4FMPD (From Ref 43)

important to know the reaction mechanism in order to synthesize high-molecular-weight fluorinated polyimides. Some of the fluorinated polyimides are soluble in certain solvents, and this characteristic has been used to determine the reaction mechanism of fluorinated polyimide synthesis by NMR measurements

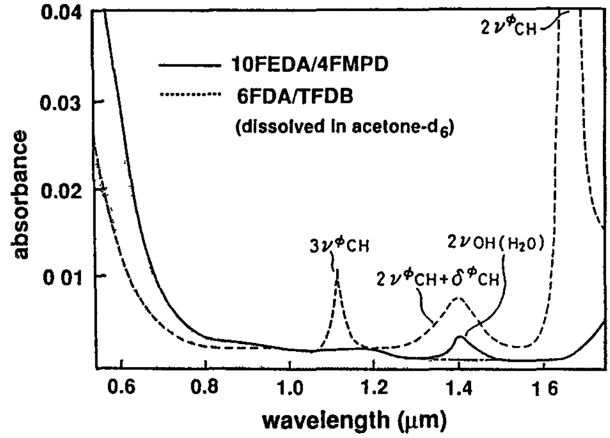


Figure 32 Visible-near-infrared absorption spectra of 10FEDA/4FMPD and 6FDA/TFDB polyimides dissolved in acetone-d_6 (From Ref 44)

In the future, fluorinated polyimide studies will receive more attention, and fluorinated polyimides designed for both electrical and optelectrical applications are expected to become a key material, for example, in integrated communication systems

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