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Polymer 40 (1999) 1411–1419

polymer

Novel perfluorononenyloxy group-containing polyimides

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Received 26 February 1998; revised 27 April 1998; accepted 27 April 1998

Abstract

A series of novel polyimides have been synthesized from the condensation of 5-(perfluorononenyloxy)isophthalic acid bis(4-aminophenyl) ester (**IV**$_3$) with various aromatic tetracarboxylic dianhydrides. For comparison, the polyimides containing the bis(4-aminophenyl) ester unit were prepared from terephthalic acid bis(4-aminophenyl) ester (**IV**$_1$) and isophthalic acid bis(4-aminophenyl) ester (**IV**$_2$) with dianhydrides. The poly(amic acid)s had inherent viscosities of 0.97–1.98 dl g^{-1}, depending on the diamines and dianhydrides. Perfluorononenyloxy group-containing polyimides (**VII**$_{3a-d}$) had lower dielectric constant (ranged from 2.73 to 2.56), lower moisture absorption, and better solubility than those of analogous polyimides (**VII1a–d**, **VII2a–d**) which do not contain perfluorononenyloxy group. Moreover, they maintained good mechanical properties (G' close to 10^9 Pa) up to 270°C. The glass transition temperatures of these perfluorononenyloxy groups containing polyimides were in the range of 268–287°C by d.s.c. and 272–291°C by d.m.a., and the 10% weight loss temperatures in nitrogen and air were above 529 and 522°C, respectively. © 1998 Elsevier Science Ltd. All rights reserved.

Keywords: 5-(Perfluorononenyloxy)isothalic acid bis(4-aminophenyl) ester; Polyimides; Poly(amic acid)s

1. Introduction

Aromatic polyimides have found wide application in the aviation, automobile, aerospace and electronic fields due to their superior electrical and mechanical behaviour, high thermal and chemical resistance and dimensional stability. Much attention has been focused recently on the preparation of fluorine-containing aromatic condensation polymers because of their unique properties and high performance [1–5]. As is well known, the fluorine atoms have special features, such as high electronegativity, large C–F bond energy, small polarizability, and low intermolecular cohesive energy. The incorporation of fluorine atoms into polymer structures has been intensively explored in the past decade with the hope of fine-tuning several properties of particular interest. It is known that the increase in solubility, processability, transparency and the decrease in dielectric constant and moisture absorption can be achieved by the incorporation of fluorine atoms into the polymers [6–21].

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 [22]. For application as an insulator in packaging, the material must possess good mechanical properties over the processing temperature and, most importantly in the context of the work reported here, the solubility must be good and the dielectric constant and moisture absorption must be as low as possible. Since signal propagation speed and wiring density in multichip packaging are dependent on the dielectric constant, considerable effort has been expended in the last decade to design and synthesize new polyimides with low dielectric constants.

Recently, we have reported the synthesis of a series of novel aromatic polyamides via direct polycondensation of 5-(perfluorononenyloxy)-isophthalic acid (**I**) with various aromatic diamines [23]. In addition, we also have reported the synthesis of a series of polyarylates via high-temperature solution condensation of 5-(perfluorononenyloxy)isophthaloyl chloride (**II**) with various aromatic diols in *o*-dichlorobenzene [24]. Transparent and flexible films of these polymers were obtained with good thermal stability and excellent mechanical properties. In this study, a synthesis of 5-(perfluorononenyloxy)isophthalic acid bis(4-aminophenyl) ester (**IV**$_3$) was performed. From **IV**$_3$ and various aromatic dianhydrides, a series of novel perfluorononenyloxy group-containing polyimides were synthesized by the usual two-step procedure that included ring-opening

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PII: S0032-3861(98)00376-0

polyaddition to give poly(amic acid)s, followed by cyclodehydration to polyimides. For comparison, we also synthesized another two bis(4-aminophenyl) ester unit containing diamines, terephthalic acid bis(4-aminophenyl) ester ($\mathbf{IV_1}$) and isophthalic acid bis(4-aminophenyl) ester ($\mathbf{IV_2}$). The polyimides containing the bis(4-aminophenyl) ester unit were then prepared. The primary aim of this work was to illustrate the effect of perfluorononenyloxy group on the properties of polyimides, such as inherent viscosity, solubility, thermal properties, dielectric constant and moisture absorption.

2. Experimental

2.1. Materials

5-Hydroxyisophthalic acid (from Aldrich), hexafluoropropene trimer (from Aldrich), triethyl amine (from Ferak), 4-nitrophenol (from TCI), terephthaloyl chloride (from Janssen), isophthaloyl chloride (from Janssen), 10% Pd/C (from Ferak), and glacial acetic acid (from Acros) were used as received. Pyromellitic dianhydride (PMDA; from Chriskev), 3,3′,4,4′-biphenyltetracarboxylic dianhydride (BPDA; from Chriskev), 3,3′,4,4′-benzophenonetetracarboxylic dianhydride (BTDA; from Chriskev), 4,4′-(hexafluoroisopropylidene)diphthalic anhydride (6FDA; from Aldrich) were recrystallized from acetic anhydride before use. *N*,*N*-Dimethylformamide (DMF) and *N*,*N*-dimethylacetamide (DMAc) were purified by distillation under reduced pressure over calcium hydride and stored over 4 Å molecular sieves. All other solvents were obtained from various commercial sources and used without further purification.

2.2. Synthesis of 5-(perfluorononenyloxy)isophthalic acid (I)

5-(Perfluorononenyloxy) isophthalic acid (**I**) was synthesized according to the method reported [23,25], m.p. 321–322°C, yield 81.2%.

2.3. Synthesis of 5-(perfluorononenyloxy)isophthaloyl chloride (II)

5-(Perfluoro-nonenyloxy)isophthalic acid (**I**) 12.24g (0.02 mol), 4 ml of DMF and 50 ml of toluene were introduced into the four-neck flask, and the mixture was preheated to 70°C. The thionyl chloride (30 ml) was then added dropwise to the flask over a period of 30 min. After the addition was completed, the mixture was heated at 80°C for another 8 h. The thionyl chloride was first removed under reduced pressure and toluene was then removed by rotary evaporator, and the residual crude product was purified by vacuum sublimation. White needles (m.p. 42–43°C) of **II** were obtained. The yield was 10.9 g (84.0%). The infrared (i.r.) spectrum (KBr) exhibited absorptions at 1780 cm^{-1} (C=O) and 987 cm^{-1} (COCl). ^{19}F n.m.r. (DMSO-d_6) δ (ppm): 6.02 (d, 3F, CF_3), −9.15 (s, 6F, CF_3), −10.32 (d, 6F, CF_3), −105.58 (quart., 1F, CF), −107.72 (quint., 1F, CF). Anal. calcd for $C_{29}H_{15}F_{17}N_2O_5$: C, 43.85%; H, 1.90%; N, 3.53%; found: C, 43.87%; H, 1.94%; N, 3.55%.

2.4. Synthesis of 5-(perfluorononenyloxy)isophthalic acid bis(4-nitrophenyl) ester ($\mathbf{III_3}$)

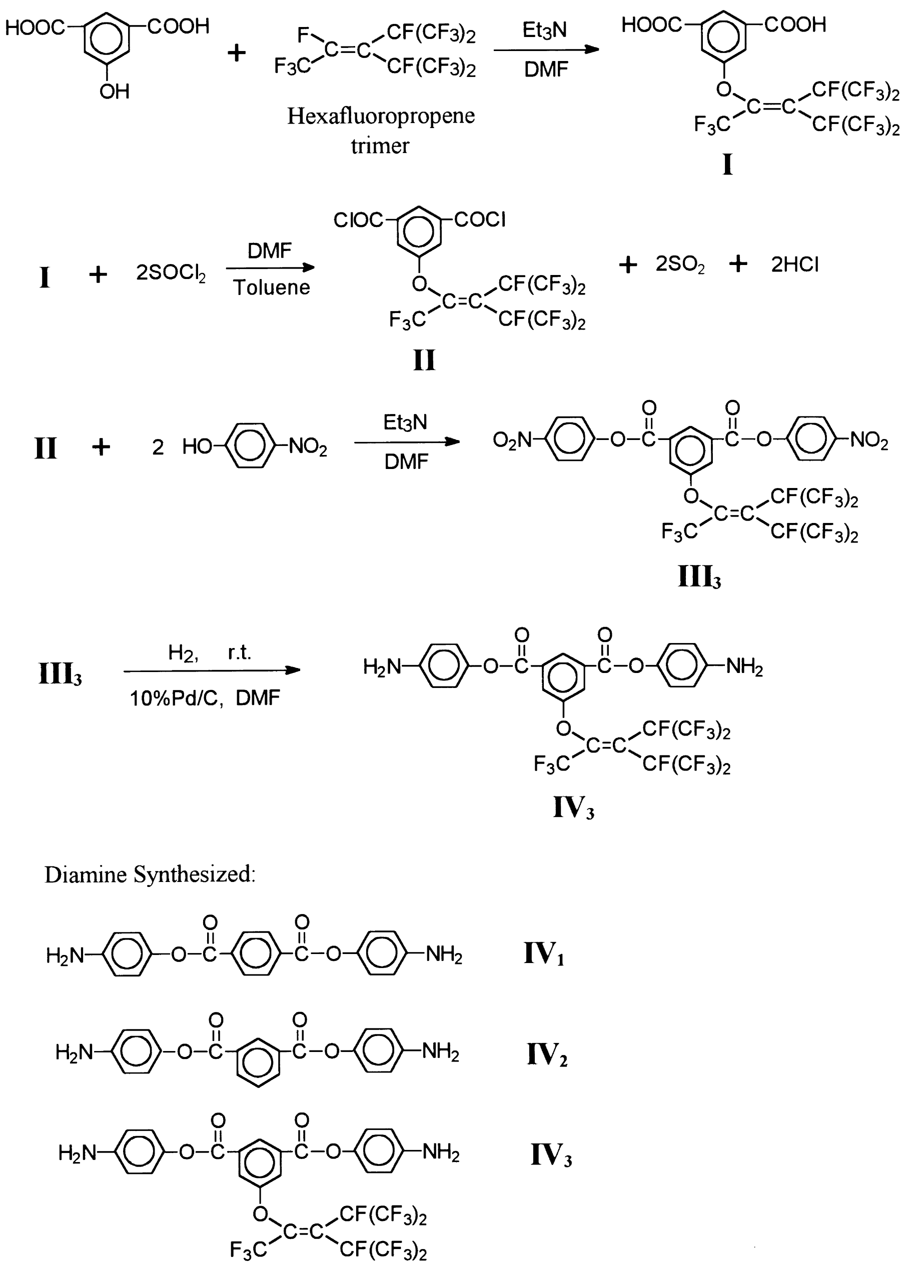
4-Nitrophenol 6.12 g (0.044 mol), 10 ml triethyl amine and the diacid chloride compound (**II**) 12.98 g (0.02 mol), which is dissolved in 50 ml DMF, were introduced into the four-neck flask with agitation at room temperature for 2 h and heated at 60°C for another 2 h. The mixture was then cooled and poured into 400 ml of methanol–water (1:1, by volume). The crude product was recrystallized from glacial acetic acid to provide white needles in 92.1% yield (m.p. 215–216°C). The i.r. spectrum (KBr) exhibited absorptions at 1516 and 1345 cm^{-1} (NO_2), 1740 cm^{-1} (C=O). ^{1}H n.m.r. (DMSO-*d*6) δ (ppm): 8.69 (s, 1H), 8.37 (s, 2H), 6.92 (d, 4H), 6.60 (d, 4H). Anal. calcd for $C_{29}H_{11}F_{17}N_2O_8$: C, 40.77%; H, 1.30%; N, 3.28%; found: C, 40.79%; H, 1.31%; N, 3.24%.

2.5. Synthesis of 5-(perfluorononenyloxy)isophthalic acid bis(4-aminophenyl) ester ($\mathbf{IV_3}$)

The dinitro compound ($\mathbf{III_3}$) 17.09 g (0.02 mol), 0.15 g of 10% Pd/C, and 35 ml of DMF were introduced into the Miniclave (a glass pressure reactor, Bchiglasuster, Switzerland) at room temperature. The Miniclave was placed on a magnetic stirrer to agitate the contents. The reaction system must be purged with nitrogen at least for 1 min before the hydrogen reduction, and the pressure was kept at about 6 kg cm^{-2} under hydrogen for 8 h. The reaction solution was then filtered to remove Pd/C. The filtered liquid thus obtained was poured into 500 ml of stirring water, giving rise to a precipitate, and then isolated by filtration, followed by recrystallization from methanol to provide white needles (m.p. 204–205°). The yield was 14.63 g (93.4%). The i.r. spectrum (KBr) showed absorptions at 3421 and 3341 cm^{-1} (N(H), 1738 cm^{-1} (C=O). ^{1}H n.m.r. (DMSO-d_6) δ (ppm): 8.71 (s, 1H), 8.38 (s, 2H), 6.93 (d, 4H), 5.09 (s, broad, 4H, amino). ^{19}F n.m.r. (DMSO-d_6) δ (ppm): 6.00 (d, 3F, CF_3), − 9.14 (s, 6F, CF_3), − 10.32 (d, 6F, CF_3), − 105.58 (quart., 1F, CF), − 107.82 (quint., 1F, CF). Anal. calcd for $C_{29}H_{15}F_{17}N_2O_5$: C, 43.85%; H, 1.90%; N, 3.53%; found: C, 43.87%; H, 1.94%; N, 3.55%. The reactions are shown in Scheme 1.

2.6. Synthesis of terephthalic acid bis(4-nitrophenyl) ester ($\mathbf{III_1}$)

This compound was prepared from the terephthaloyl chloride with 4-nitrophenol in the presence of triethyl



Scheme 1.

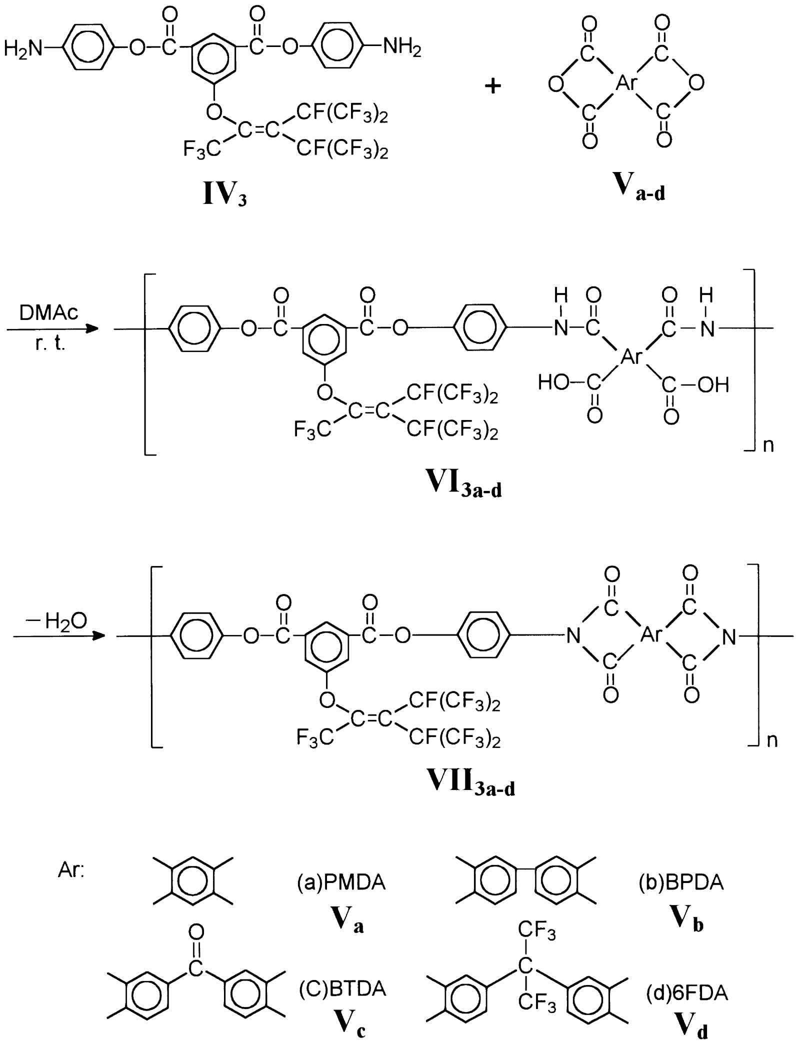
amine and DMF. The crude product was recrystallized from glacial acetic acid to give white needles (m.p. 240–241°C). The i.r. spectrum (KBr) exhibited absorptions at 1522 and 1347 cm^{-1} (NO_2) and 1741 cm^{-1} (C=O). Anal. calcd for $C_{20}H_{12}N_2O_8$: C, 58.83%; H, 2.96%; N, 6.86%; found: C, 58.87%; H, 3.00%; N, 6.85%.

2.7. *Synthesis of terephthalic acid bis(4-aminophenyl) ester (**IV**$_1$)*

This compound was prepared by reducing the dinitro compound (**III**$_1$) with hydrogen. The procedure was the same as mentioned above. The crude product was recrystallized from methanol to give gray-white needles (m.p. 232–233°C). The i.r. spectrum (KBr) showed absorptions at 3460 and 3371 cm^{-1} (N(H), 1725 cm^{-1} (C=O). ^1H n.m.r. (DMSO-d_6) δ (ppm): 8.24 (s, 4H), 6.93 (d, 4H), 6.58 (d, 4H), 5.09 (s, 4H, amino). Anal. calcd for $C_{20}H_{16}N_2O_4$: C, 68.96%; H, 4.63%; N, 8.04%; found: C, 69.01%; H, 4.65%; N, 8.07%.

2.8. *Synthesis of isophthalic acid bis(4-nitrophenyl) ester (**III**$_2$)*

This compound was prepared from the isophthaloyl chloride with 4-nitrophenol in the presence of triethyl



Scheme 2.

amine and DMF. The crude product was recrystallized from glacial acetic acid to give white needles (m.p. 226–227°C). The i.r. spectrum (KBr) exhibited absorptions at 1522 and 1350 cm^{-1} (NO_2) and 1744 cm^{-1} (C=O). Anal. calcd for $C_{20}H_{12}N_2O_8$: C, 58.83%; H, 2.96%; N, 6.86%; found: C, 58.89%; H, 2.97%; N, 6.88%.

2.9. Synthesis of isophthalic acid bis(4-aminophenyl) ester (**IV**$_2$)

This compound was prepared by reducing the dinitro compound (**III**$_2$) with hydrogen. The procedure was the same as mentioned above. The crude product was recrystallized from methanol to give white needles (m.p. 216–217°C). The i.r. spectrum (KBr) showed absorptions at 3424 and 3345 cm^{-1} (N(H), 1738 cm^{-1} (C=O). ^{1}H n.m.r. (DMSO-d_6) δ (ppm): 8.71 (s, 1H), 8.38 (d, 2H), 7.81 (t, 1H), 6.94 (d, 4H), 6.61 (d, 4H), 5.08 (s, broad, 4H, amino). Anal. calcd for $C_{20}H_{16}N_2O_4$: C, 68.96%; H, 4.63%; N, 8.04%; found: C, 68.94%; H, 4.66%; N, 8.01%.

2.10. Polymerization

A typical example of the polycondensation is given below and the reaction is shown in Scheme 2.

2.11. Polyimide **VII**$_{3a}$ from diamine **IV**$_3$ and dianhydride **V**$_a$ (**PMDA**)

5-(Perfluorononenyloxy)isophthalic acid bis(4-aminophenyl) ester (**IV**$_3$) 1.946 g (2.450 mmol) was dissolved in DMAc (15 ml) to give a clear solution, and PMDA 0.534 g (2.450 mmol) was then added to the solution with vigorous stirring. The solution was stirred in a dry nitrogen atmosphere at room temperature for 4 h, and the 15 wt% poly(amic acid) **VI**$_{3a}$ was obtained. The poly(amic acid) solution was trickled into 500 ml of isopropanol–water (1:1 by volume), giving rise to a precipitate which was washed thoroughly with isopropanol and water, collected by filtration, and dried. The inherent viscosity of the poly(amic acid) in DMAc was 1.98 dl g^{-1}, measured at a concentration of 0.5 g dl^{-1} at 30°C. The i.r. spectrum showed an absorption peak due to carbonyl stretching of the amide group which appeared at about 1725 cm^{-1} in the poly(amic acid). The poly(amic acid) solution thus obtained was cast onto a glass plate and the solvent was removed at 80°C in a vacuum oven for 2 h. The semi-dried film was further dried and imidized by sequential heating at 120°C for 30 min, 150°C for 30 min, 180°C for 30 min, and 300°C for 1 h. This treatment promoted imidization and converted poly(amic acid) into polyimide. The resulting polyimide film obtained by the thermal treatment was insoluble in DMAc and other aprotic solvents but soluble in concentrated sulfuric acid. The i.r. spectrum of the polyimide (film) exhibited absorption peaks due to carbonyl asymmetric and symmetric stretching of imide groups which appeared at 1730 and 1785 cm^{-1}.

2.12. Measurements

The i.r. spectra were measured with a Jasco VALOR III spectrometer. In a typical experiment, an average of 20 scans per sample was made. The ^{1}H n.m.r. spectra were measured with a Bruker WP-100 n.m.r. spectrometer at 200 MHz, using dimethyl-*d*6 sulfoxide as a solvent. The ^{1}H chemical shifts were calibrated by using tetramethylsilane (TMS) as an internal standard. The ^{19}F n.m.r. spectrum was measured with a Bruker AMX-400 n.m.r. spectrometer at 376.43 MHz, using dimethyl-d_6 sulfoxide as a solvent. The ^{19}F chemical shifts were calibrated by using benzotrifluoride as an internal standard. Elemental analyses were carried out with Heraeus CHN-Rapid element analyzer. Melting points were obtained on a polarizing microscope (Laboratory Devices MEL-TEMP. II) melting-point apparatus and were uncorrected. The inherent viscosities were measured with a Ubbelohde capillary viscometer (Schott-AVS310). D.s.c. data were obtained from 8 to 10 mg samples in a nitrogen atmosphere at a flow rate of 30 cm^3 min^{-1} and a heating rate of 20°C min^{-1} using a DuPont 910 d.s.c. Thermogravimetric analyses (t.g.a.) were performed on a DuPont 951 thermal analyzer using a heating rate of 20°C min^{-1} in N_2 at a flow rate of 50 cm^3 min^{-1}. The dielectric constants were measured with a DuPont DEA 2970 (dielectric analyzer) at a frequency of 1 kHz and a temperature 30°C in a nitrogen atmosphere at a flow rate of 500 cm^3 min^{-1} by the two parallel plate mode. The specimens were subjected to vacuum pretreatment of 1 Torr at 120°C for 4 h to eliminate absorbed water. Dynamic mechanical analyses (d.m.a.) were made with a Perkin-Elmer DMA 7e. The storage modulus G' and tan δ were studied when the sample was subjected to temperature scan mode at a programmed heating rate of 5°C min^{-1} from ambient to 350°C at a frequency of 1 Hz and an amplitude of 0.2 mm. A sample 10 mm in length, 2 mm in width, and approximately 0.1 mm in thickness was used. The wide-angle x-ray measurements were performed at room temperature with film specimens about 0.2 mm thick on a Rigaku Geiger Flex D-Max IIIa x-ray diffractometer, using Ni-filtered Cu Kα radiation (40 kV, 15 mA). The scanning rate was 4° min^{-1}. Qualitative solubility was determined using 0.01 g of polymer in 2 ml of solvent. The amounts of moisture absorption were measured by immersing specimens in 25°C water for 3 days and calculated the weight differences.

3. Results and discussion

3.1. Monomers synthesis

5-(Perfluorononenyloxy)isophthalic acid (**I**) was synthesized from 5-hydroxyisophthalic acid and hexafluoropropene trimer. 5-(Perfluorononenyloxy)isophthaloyl chloride (**II**) was prepared from (**I**) with thionyl chloride in 84.0% yield. The structure of **II** were confirmed by elemental analysis, i.r. and ^{19}F n.m.r. spectroscopy. The results were in good agreement with the proposed structure.

The 5-(perfluorononenyloxy)isophthalic acid bis(4-nitrophenyl) ester (**III$_3$**) was prepared from diacid chloride (**II**) with 4-nitrophenol in 92.1% yield. Reduction of the dinitro compound to an amino compound can be carried out in a number of ways, e.g., the catalytic hydrogenation (H_2/Pd-C), the acid (HCl) and metal or metal salt, or hydrazine hydrate/Pd-C. In the present work, the dinitro compound (**III$_3$**) was catalytically hydrogenated with Pd/C since this method led to higher yields than the corresponding reduction carried out with hydrazine hydrate and also did not break the ester group of the dinitro compound during reduction. The structures of intermediate dinitro compound and diamine were confirmed by i.r., ^{1}H and ^{19}F n.m.r. spectroscopy, and elemental analysis.

3.2. Preparation of polymers

Polyimides were synthesized by a conventional two-step polycondensation of a dianhydride and a diamine in an aprotic solvent such as DMAc. The ring-opening polyaddition in DMAc at room temperature afforded poly(amic acid)s which was cyclodehydrated to polyimides. The polyimide films were pale yellow, transparent, and flexible.

The inherent viscosities of poly(amic acid)s and their corresponding polyimides are summarized in Table 1. The poly(amic acid)s had inherent viscosities in the range 0.97–1.98 dl g^{-1}, suggesting the formation of high-molecular weight polymers. Among them, the poly(amic acid)s **VII$_{1a,2a,3a}$** derived from PMDA exhibited higher inherent viscosity than those of **VII$_{1d,2d,3d}$** derived from 6FDA because of its rigid-rod main chains and/or its higher molecular weight. The inherent viscosities of the polyimides measured in concentrated sulfuric acid ranged from 0.71 to 1.03 dl g^{-1}.

In general, the steric and electronic characteristics of the fluorinated groups can reduce the reactivity of the

Table 1
Synthesis of poly(amic acid)s and polyimides

Poly(amic acid)s		Polyimides	
Code	η^{a}_{inh} (dl g^{-1})	Code	η^{b}_{inh} (dl g^{-1})
VI$_{1a}$	1.75	**VII**$_{1a}$	1.03
VI$_{1b}$	1.12	**VII**$_{1b}$	0.71
VI$_{1c}$	1.19	**VII**$_{1c}$	0.78
VI$_{1d}$	1.09	**VII**$_{1d}$	0.73
VI$_{2a}$	1.63	**VII**$_{2a}$	1.01
VI$_{2b}$	1.04	**VII**$_{2b}$	0.85
VI$_{2c}$	1.15	**VII**$_{2c}$	0.92
VI$_{2d}$	0.97	**VII**$_{2d}$	0.71
VI$_{3a}$	1.98	**VII**$_{3a}$	1.02
VI$_{3b}$	1.18	**VII**$_{3b}$	0.81
VI$_{3c}$	1.23	**VII**$_{3c}$	0.85
VI$_{3d}$	1.05	**VII**$_{3d}$	0.79

[a] Measured in DMAc at a concentration of 0.5 g dl^{-1} at 30°C
[b] Measured in concentrated sulfuric acid at a concentration of 0.5 g dl^{-1} at 30°C

nucleophilic component of a polycondensation reaction to the point where polymerization is suppressed or effectively precluded. The inherent viscosities of poly(amic acid)s **VI**$_{3a-d}$ and polyimides **VII**$_{3a-d}$ prepared from perfluorononenyloxy group-containing diamine were not lower than those of **VI**$_{1a-2d}$ and **VII**$_{1a-2d}$, which were synthesized from **IV**$_1$ and **IV**$_2$. Elemental analyses of these polyimides are generally in good agreement with the calculated values based on the polymer repeating units.

3.3. Properties of polymers

The solubility of these polyimides were tested in various solvents, and the results are summarized in Table 2. Polyimides **VII**$_{1a-2d}$ were thoroughly soluble only in concentrated sulfuric acid. Polyimides **VII**$_{3a-d}$ containing perfluorononenyloxy group, however, were much more soluble than others. This can be explained by the reduction in chain–chain interaction in polyimide **VII**$_{3a-d}$, since fluorine has low intermolecular attractive forces. The higher solubility is also attributed to the introduction of bulky perfluorononenyloxy group to the polymer backbone.

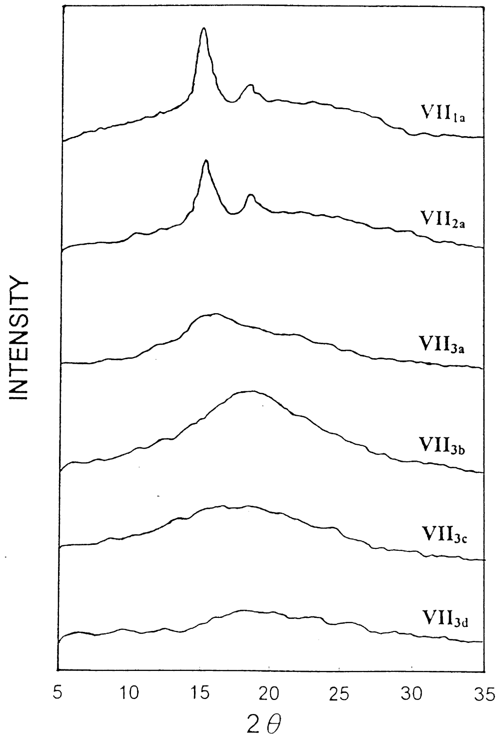


Fig. 1. Wide-angle x-ray diffractograms of some polyimides.

The crystallinity of the polyimide films was evaluated by x-ray diffraction analysis with 2θ ranging from 5 to 35°. As shown in Fig. 1, polyimides **VII**$_{1a}$ and **VII**$_{2a}$ showed crystalline character and exhibited two strong peaks around 15 and 20°, which may be due to the more efficient packing of polymer chains containing polypyromellitimide. Polyimide **VII**$_{3a}$ exhibited an amorphous pattern. In general, most of

Table 2
Solubility of polyimides[a]

Polymer	Solvent[b]							
	DMAc	DMF	DMSO	NMP	*m*-Cresol	*o*-Chlorophenol	Pyridine	Conc. H$_2$SO$_4$
VII$_{1a}$	−	−	−	−	−	−	−	+
VII$_{1b}$	−	−	−	−	−	−	−	+
VII$_{1c}$	−	−	−	− h	−	−	−	+
VII$_{1d}$	−	−	−	− h	− h	− h	−	+
VII$_{2a}$	−	−	−	−	−	−	−	+
VII$_{2b}$	−	−	−	−	−	− h	−	+
VII$_{2c}$	−	−	−	− h	−	− h	−	+
VII$_{2d}$	− h	− h	− h	− h	− h	− h	− h	+
VII$_{3a}$	− h	− h	− h	− h	− h	− h	− h	+
VII$_{3b}$	− h	− h	− h	− h	− h	+ h	− h	+
VII$_{3c}$	+ h	− h	+ h	+ h	− h	+ h	− h	+
VII$_{3d}$	+ h	+ h	+ h	+ h	− h	+ h	+ h	+

[a] Solubility: + , soluble at room temperature; + h soluble on heating; − h, partially soluble on heating; − , insoluble
[b] DMAc, *N*,*N*-dimethylacetamide; DMF, *N*,*N*-dimethylformamide; DMSO, dimethyl sulfoxide; NMP, *N*-methyl-2-pyrrolidone

Table 3
Thermal properties of polyimides

Polymer	T_g^a (°C)			Decomposition temperature^c (°C)		Char yield^d (%)
	D.s.c.	D.m.a.	T_m^b (°C)	In N_2	In air	
$\mathbf{VII}_{1a}$	303	306	372	565	558	601
$\mathbf{VII}_{1b}$	292	294	—^{e}	567	560	63.7
$\mathbf{VII}_{1c}$	283	286	—	556	547	58.3
$\mathbf{VII}_{1d}$	271	278	—	551	546	58.9
$\mathbf{VII}_{2a}$	295	297	364	561	554	58.2
$\mathbf{VII}_{2b}$	279	283	—	557	553	65.3
$\mathbf{VII}_{2c}$	275	279	—	548	537	57.6
$\mathbf{VII}_{2d}$	269	273	—	541	531	57.9
$\mathbf{VII}_{3a}$	287	291	—	554	542	55.6
$\mathbf{VII}_{3b}$	275	278	—	549	541	63.2
$\mathbf{VII}_{3c}$	271	275	—	538	533	59.5
$\mathbf{VII}_{3d}$	268	272	—	529	522	58.9

[a] Glass transition temperature (T_g) measured by d.s.c. and d.m.a. at a heating rate of 20 and 5°C min^{-1}, respectively

[b] Melting temperature measured by d.s.c. at a heating rate of 20°C min^{-1}. Temperature at 10% weight loss recorded by t.g.a. at a heating rate of 20°C min^{-1}

[d] Residual weight % at 800°C in nitrogen

[e] Dashes indicate that the melting temperatures of polymers were not detected by d.s.c.

the cardopolymers are amorphous, primarily because of the bulky pendant structure. All the other polyimides showed amorphous patterns.

The thermal behaviour of these polyimides was evaluated by d.s.c., d.m.a. and t.g.a. The results are summarized in Table 3. All polyimides show a similar decomposition behaviour characterized by no weight loss below 450°C in air or in nitrogen, and the 10% weight loss temperatures were in the range 529–567°C in nitrogen and 522–560°C in air depending on the diamines and dianhydrides used. Polyimides based on PMDA and BPDA exhibit higher thermal stability. The 10% weight loss temperature of polyimides $\mathbf{VII}_{3a-d}$ in air is about 7–11°C lower than that in nitrogen, indicating perfluorononenyloxy group-containing polyimides showed thermooxidative stability in air. The amount of carbonized residue of polyimide $\mathbf{VII}_{3a-d}$ at 800°C in nitrogen atmosphere was higher than 55%; the polyimide $\mathbf{VII}_{3b}$ had the highest char yield of up to 63.2%.

Since the residual water or solvent and the history of thermal annealing have sometimes influenced the first heating run of d.s.c., samples were at first heated to 250°C and the T_g was determined by the second heating. In the d.m.a. measurement, the peak of tan δ was identified as the T_g. The polymers have glass transition temperatures of 268–303°C by d.s.c. and 272–306°C by d.m.a. The T_g values tend to decrease in the order $\mathbf{VII}_{3a} > \mathbf{VII}_{3b} > \mathbf{VII}_{3c} > \mathbf{VII}_{3d}$, which is consistent with the decreasing order of stiffness and polarity of the polymer backbone. Table 3 also reveals that the glass transition temperature or 10% weight loss temperature of perfluorononenyloxy group-containing polyimides $\mathbf{VII}_{3a-d}$ are slightly lower than those of analogous polyimides $\mathbf{VII}_{1a-d}$ and $\mathbf{VII}_{2a-d}$. It is evident that the effect of perfluorononenyloxy group on the thermal properties in the present work is small.

The dynamic mechanical properties of polymers $\mathbf{VII}_{3a-d}$ are indicated in Fig. 2. All the perfluorononenyloxy group-containing polyimides showed similar d.m.a. curves and maintained good mechanical properties (G' close to 109 Pa) up to temperatures close to glass transition well above 270°C. The storage moduli tended to decrease in the order $\mathbf{VII}_{3a} > \mathbf{VII}_{3b} > \mathbf{VII}_{3c} > \mathbf{VII}_{3d}$ and the tan δ values tended to increase in the order $\mathbf{VII}_{3a} < \mathbf{VII}_{3b} < \mathbf{VII}_{3c} < \mathbf{VII}_{3d}$. These results were quite compatible with the decreasing order of stiffness and rigidity of the polymer backbone.

The dielectric constants of polyimides are shown in Table 4. The dielectric constant of each material was measured under two conditions. The wet dielectric constant at 1 kHz was measured after equilibration at 70% relative humidity, and the dry dielectric constant at 1 kHz was measured after the specimens were subjected to vacuum pretreatment of 1 Torr at 120°C for 4 h to eliminate

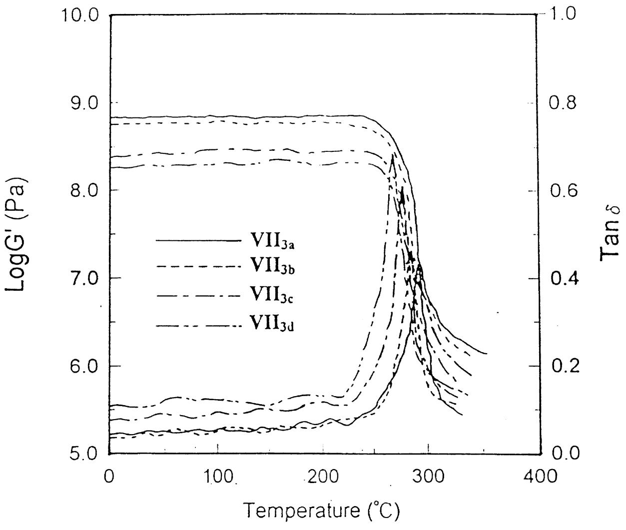


Fig. 2. Dynamic mechanical analysis curves for $\mathbf{VII}_{3a-d}$ films at a heating rate of 5 min^{-1}.

Table 4
Dielectric constant and moisture absorption of polyimides

Polymer	Wet dielectric constant[a]	Dry dielectric constant[b]	Moisture absorbtion (%)[c]
$\mathbf{VII}_{\mathbf{1a}}$	3.87	3.31	0.92
$\mathbf{VII}_{\mathbf{1b}}$	3.74	3.28	0.83
$\mathbf{VII}_{\mathbf{1c}}$	3.72	3.23	0.84
$\mathbf{VII}_{\mathbf{1d}}$	3.51	3.14	0.49
$\mathbf{VII}_{\mathbf{2a}}$	3.94	3.35	0.89
$\mathbf{VII}_{\mathbf{2b}}$	3.81	3.31	0.78
$\mathbf{VII}_{\mathbf{2c}}$	3.78	3.27	0.76
$\mathbf{VII}_{\mathbf{2d}}$	3.54	3.17	0.48
$\mathbf{VII}_{\mathbf{3a}}$	2.89	2.73	0.24
$\mathbf{VII}_{\mathbf{3b}}$	2.82	2.68	0.23
$\mathbf{VII}_{\mathbf{3c}}$	2.84	2.66	0.25
$\mathbf{VII}_{\mathbf{3d}}$	2.61	2.56	0.18

[a] Measured by d.e.a. at 1 kHz after equilibration at 70% relative humidity, 30°C
[b] Measured by d.e.a. at 1 kHz after exhaustive drying, 30°C
[c] Specimens were immersed in water at 25°C, and the weight differences after 3 days were measured

absorbed water. Perfluorononenyloxy group-containing polyimides $\mathbf{VII}_{\mathbf{3a-d}}$ had much lower dry dielectric constants, ranging from 2.73 to 2.56, than other polyimides in the present work. It is evident that several factors contribute to the decrease in the dielectric constant. The presence of bulky perfluorononenyloxy groups between imide linkages may reduce interchain electronic interaction thus decreasing the dielectric constant. The presence of fluoro substituents may cause steric changes, resulting in a less efficient chain packaging and an increase in the free volume of the polymer, bringing the dielectric constant closer to the value of air and/or reducing the number of polarizable groups in a unit volume. In addition, fluorine may affect a decrease in the electronic polarization due to the smaller electronic polarizability of the C–F bond relative to C–H, thus decreasing the dielectric constant.

On the other hand, the strong electron-attracting property, resulting from the high electronegativity of the fluorine atom, could produce additional permanent dipole in the perfluorononenyloxy group and/or the benzene ring connected to the perfluorononenyloxy group. These dipoles may increase the polarization, and hence the dielectric constant. The experimental data on dielectric constant indicate that the effect of these additional permanent dipoles is smaller than the other effects, i.e., the chain–chain interaction, free volume, and the electronic polarization in polyimide.

Table 4 also presents the moisture absorption (%) of polyimide films. The lower moisture absorption characteristics of the resulting polymers $\mathbf{VII}_{\mathbf{3a-d}}$ may be attributed to the presence of hydrophobic perfluorononenyloxy groups on the surface of polyimide films and also to the low affinity of fluorine atoms toward water. Moreover, the dielectric constants taken after equilibration at 70% relative humidity show a larger increase relative to the dry data in polyimide $\mathbf{VII}_{\mathbf{1a-2d}}$ than the perfluorononenyloxy group-containing polyimides. This is a clear indication that the hydrophobicity of the polymers leads to differences between the wet dielectric constant and dry dielectric constant.

4. Conclusions

5-(Perfluorononenyloxy)isophthalic acid bis(4-aminophenyl) ester (**IV3**) has been synthesized. A series of novel perfluorononenyloxy group-containing polyimides were prepared from $\mathbf{IV}_{\mathbf{3}}$ with various aromatic dianhydrides. Polyimides based on $\mathbf{IV}_{\mathbf{3}}$ were shown to have valuable properties, such as low dielectric constant, low moisture absorption, and good solubility for electronic applications. Moreover, perfluorononenyloxy group-containing polyimides possess good thermal properties and excellent mechanical properties.

Acknowledgements

We are grateful to the National Science Council of the Republic of China for the support of this work (Grant NSC 87-2214-E006-028).

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