Synthesis and characterization of fluorinated poly(imide-pyridazine-amide)s

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New poly(imide-pyridazine-amide)s have been synthesized by the solution polycondensation of aromatic diamines containing preformed pyridazine rings with diacid chlorides which incorporate both imide and hexafluoroisopropylidene units. Solubility, thermal stability and electro-insulating properties of these compounds are discussed and compared with those of fluorinated poly(imide-amide)s which do not contain pyridazine rings, and also with those of other related heterocyclic polymers that have been previously reported.

(Keywords: poly(imide-pyridazine-amide)s; fluorinated copolymers; dielectric constant)

INTRODUCTION

Aromatic polyimides have found wide application in the electronics industry due to their superior electrical and mechanical behaviour, high thermal and chemical resistance and dimensional stability[1]. They are generally used as flexible circuitry substrates, interlayer dielectrics and passivation and protective coatings in high density electronic packaging devices. The most common method for the preparation of polyimides is a two-step polymerization process which allows the use of a soluble precursor, namely polyamic acid, to deposit thin films, followed by thermal treatment to achieve the fully cyclized structure. There are, however, certain limitations connected with the instability of polyamic acid solutions, such as completeness of cyclization, elimination of released water and formation of microvoids in the final film. Therefore, further investigations have been undertaken in order to identify new ways to circumvent these restrictions. One approach is to use monomers containing preformed imide rings and to introduce flexibilizing groups, such as amides or esters, into the main chain[2]. On the other hand, with the ever increasing sophistication in electronics devices (such as smaller sizes and faster speeds), new demands are being placed on the materials that are now being brought into these areas. Since signal propagation speed and wiring density in microelectronic packaging are dependent on the dielectric constant, a considerable effort has been expended recently in the design of new polyimides with lower dielectric constants. The greatest concentration of work towards this end has involved the incorporation of fluorine atoms in the chemical structure[3].

Continuous research is now being carried out, including the use of various copolymers containing imide and other heterocyclic units, with the aim of producing materials with a better balance of thermal and electrical properties, as well as improved processing capabilities[4].

Polyimides containing oxadiazole[5], benzoxazole[6], quinoxaline[7], benzimidazole[8], and other heterocyclic units, have been largely studied, but only very few investigations have been carried out on the introduction of pyridazine rings into the polymer chain, in addition to the imide groups[9].

As part of an effort to obtain high performance, high temperature resistant polymers for microelectronic applications, we considered it of interest to synthesize new thermostable copolymers which contain both imide and pyridazine rings, as well as flexible hexafluoroisopropylidene groups and other flexible linkages, in one macromolecular chain. Therefore, we have prepared a series of fluorinated poly(imide-pyridazine-amide)s by the solution polycondensation of aromatic diamines containing pyridazine units with diacid chlorides which incorporate both preformed imide rings and hexafluoroisopropylidene groups. The solubility, film forming ability, thermal stability and dielectric constant of these materials have been studied and compared with those of related polymers.

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EXPERIMENTAL

Starting materials

N-methyl-2-pyrrolidinone (NMP) (Merck) was distilled over phosphorous pentoxide under reduced pressure. 3,6-Dichloropyridazine, 4-aminophenol, 3-aminophenol, potassium carbonate, and *N*,*N*-dimethylacetamide (DMA) were purchased from Aldrich and used without further purification. Pyridine (Py), *N*,*N*-dimethylformamide (DMF), 4-aminobenzoic acid, 3-aminobenzoic acid, thionyl chloride and glacial acetic acid were provided by Merck and used as received.

Hexafluoroisopropylidene diphthalic anhydride was a gift from Hoechst and was used without further purification, 1,4-Bis(4-aminophenoxy)benzene was obtained from Ken Seika Corp. and was used as received.

Preparation of pyridazine-containing diamines(I)

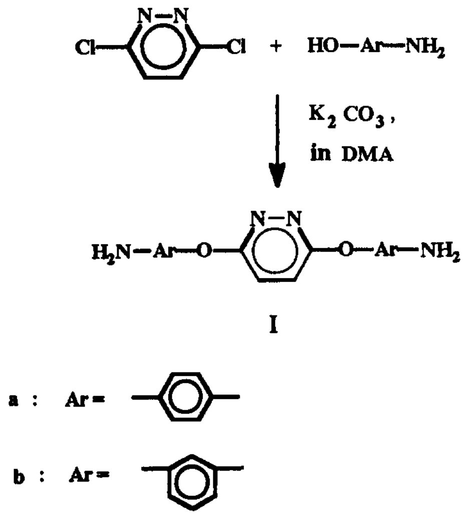
3,6-Bis(*p*-aminophenoxy)pyridazine (Ia) and 3,6-bis(*m*-aminophenoxy)pyridazine (Ib) were prepared following a method previously described[10], using 3,6-dichloropyridazine and *p*- or *m*-aminophenol in DMA with potassium carbonate, as shown in *Scheme 1* (see later).

Preparation of the diacid chlorides(II)

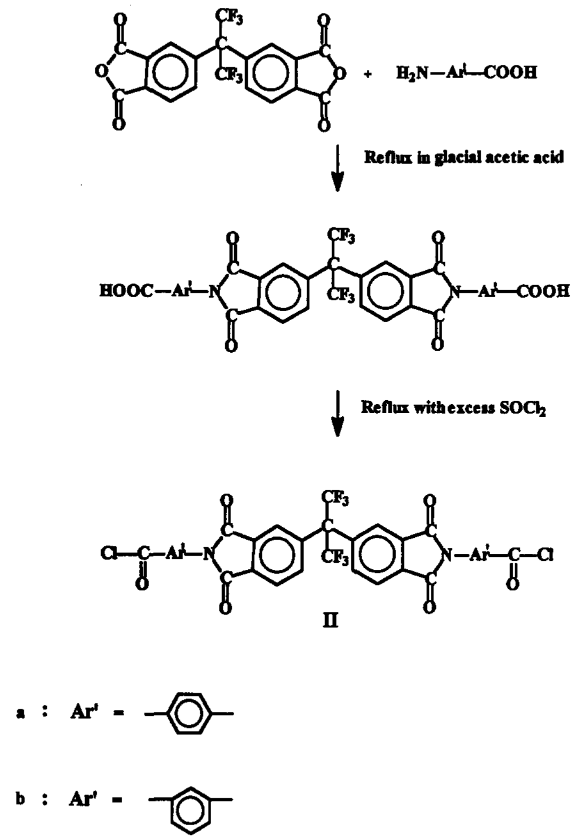
p-Aminobenzoic acid (or *m*-aminobenzoic acid) (2 mol) and hexafluoroisopropylidene diphthalic anhydride (1 mol) were reacted in refluxing glacial acetic acid to give the corresponding diimide dicarboxylic acids as white crystalline products, which were filtered, washed with ethanol and dried. They were then refluxed with excess thionyl chloride, using DMF as a catalyst, to give the diacid chlorides II as white crystalline compounds[11]. These reactions are shown in *Scheme 2*.

General polymer synthesis

The polycondensation reaction was run under anhydrous conditions, in a nitrogen atmosphere, with equimolar amounts of diamine and diacid chloride being used, in NMP as the solvent and with Py as the acid acceptor. The relative amounts of monomers and NMP were adjusted to maintain a solid content of 10 wt%. A typical reaction was carried out as follows: in a 100 ml three-necked flask, equipped with a mechanical stirrer and a N_2 gas inlet and outlet, were placed 1.47 g (0.005 mol) of Ia, 45 ml of NMP and 0.4 ml of Py, and the mixture was stirred under N_2 until complete dissolution was achieved. The solution was cooled to −10°C and 3.595 g (0.005 mol) of IIa were then added (as a fine powder) with rapid stirring. The contents of the flask were kept below 0°C for 15 min, and the cooling bath was then removed and the reaction mixture was allowed to reach room temperature, after which it was stirred for a further 4 h. Half of the resulting viscous solution was cast onto a glass plate (200 × 200 mm) and after evaporating the solvent at temperatures of 120, 160, 200 and 240°C, each for periods of 1 h, a flexible transparent film was obtained which was stripped off the plate by immersion in hot water for 2 h. It was then dried at 120°C for 1 h, at 200°C for 20 min and at 300°C for a further 20 min. The other half of the polymer solution was poured into water with rapid stirring, and the light-rose-coloured fibrous product which precipitated was filtered, washed twice with 100 ml of water, then with 100 ml of ethanol, and finally dried in an oven at 120°C for 6 h. The film was used to record the i.r. spectrum and to measure the electrical properties, while the precipitate was used for all of the other investigations.



Scheme 1 Preparation of pyridazine-containing diamines



Scheme 2 Preparation of diacid chlorides

Measurements

The inherent viscosities of the polymers were determined in NMP at 20°C, at a concentration of 0.5 g dl^{-1}, by using an Ubelohde viscometer. Infra-red spectra were recorded with a Nicolet Magna 550 FTIR spectrometer using polymer films with a thickness of 2–5 μm.

The glass transition temperatures (T_gs) of the precipitated polymers were determined with a Seico differential scanning calorimeter (DSC 220C), using a heating rate of 10°C min^{-1}. The thermal stability was investigated using a Seico TGA/DTA 220 thermobalance, operating at a heating rate of 20°C min^{-1} in air. The data were collected and analysed by using the Seico SSC 5200 data system. The initial decomposition temperature (*IDT*) is characterized as the temperature at which the samples achieve a 3% weight loss. The weight loss at 500°C in air was also recorded.

The dielectric constants were measured using the previously described fluid displacement method[12]. The capacitance of the films was measured using circular gold electrodes (diameter = 2.54 cm) mounted in a brass dielectric cell held at a constant temperature (25°C) and a Gen Rad Precision LC Digibridge (Model 1688), operating at 10 kHz. The relative humidity (*RH*) was measured by a General Eastman Dew-point Hygrometer (System 1100 DP).

RESULTS AND DISCUSSION

The pyridazine-containing diamines I were readily prepared in high yields by using a procedure reported in the literature[10]. This reaction is based on the nucleophilic displacement of the activated chlorine atoms in 3,6-dichloropyridazine by potassium phenoxide in polar aprotic solvents, such as DMA. The pyridazine moiety can accept a negative charge and lower the activation energy for the displacement of the chlorine substituent through a Meisenheimer complex, analogous to conventional activating groups such as ketone or sulfone. *Scheme 1* shows the synthesis of these diamines.

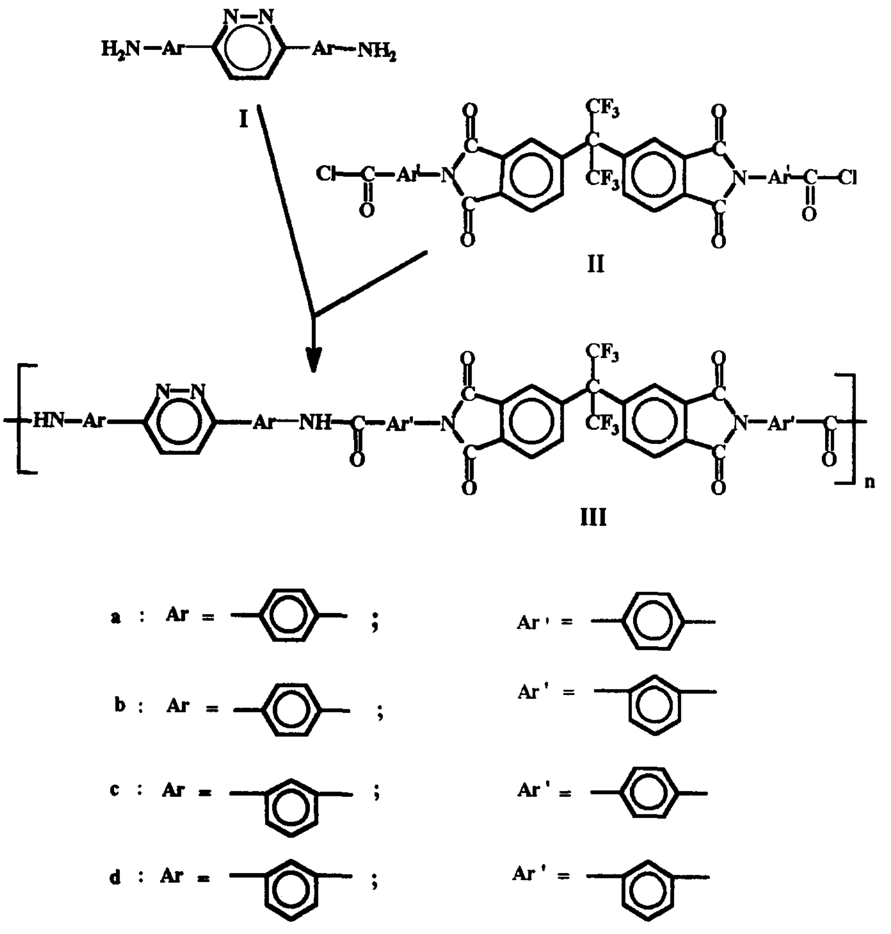
The diacid chlorides II were also easily accessible in high yields by the reaction of *p*- or *m*-aminobenzoic acid with hexafluoroisopropylidene diphthalic anhydride, resulting in the intermediate diimide dicarboxylic acids, which were then heated with thionyl chloride, as shown in *Scheme 2*.

The poly(imide-pyridazine-amide)s III were prepared by the low-temperature solution polycondensation of the pyridazine-containing diamines I with the diacid chlorides II, as depicted in *Scheme 3*.

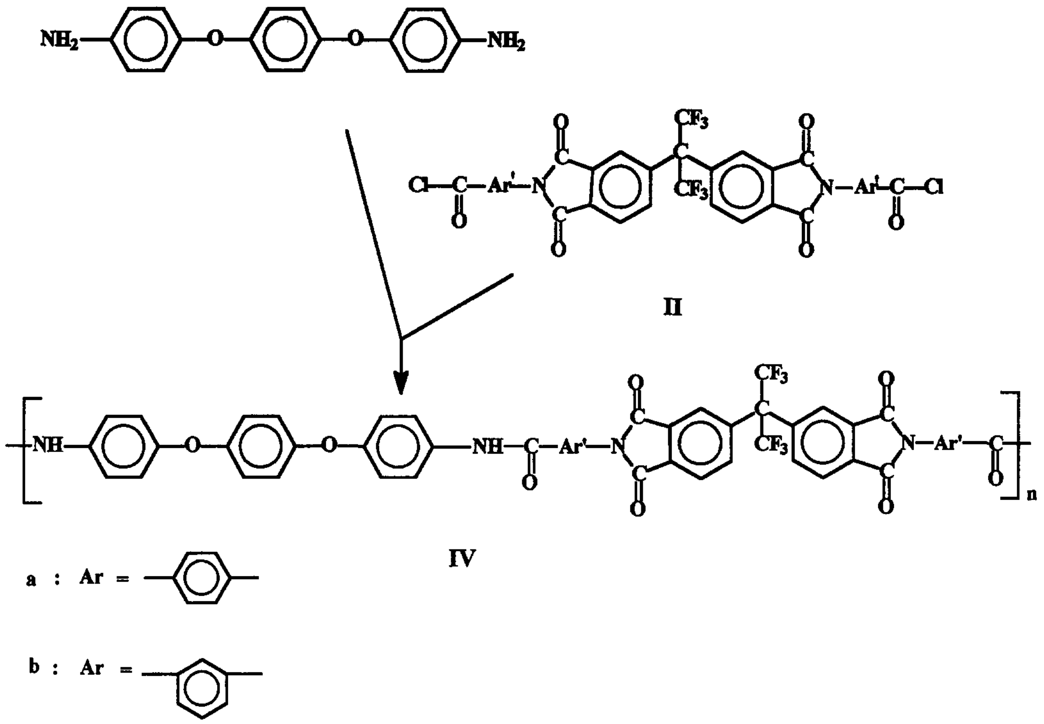
The related poly(imide-amide)s IV, which contain no pyridazine rings, were prepared by the polycondensation of commercially available 1,4-bis(*p*-aminophenoxy)benzene with the diacid chlorides II, as shown in *Scheme 4*.

These last two reactions were performed by adding the powdered diacid chloride to a cooled solution of the diamine in a mixture of NMP and Py. The clear viscous solutions which resulted after stirring first at low temperature, and then at room temperature, were used to cast thin films onto glass plates, or they were precipitated by pouring into water, followed by a thorough washing with water and ethanol.

All of the polymers synthesized as described above, easily dissolve in polar amidic solvents, such as NMP and DMF. The improved solubility of these polymers, when compared to fully aromatic polyimides, can be explained mainly by the presence of the hexafluoroisopropylidene units. The inherent viscosities of the polymers III are in the range 0.4–0.6 dl g^{-1} (*Table 1*). Compounds IIIa and IIIc have higher viscosities than IIIb and IIId, probably due to the higher reactivity of the diacid chloride IIa, when compared to IIb. A similar effect was previously observed in the reaction of these diacid chlorides with oxadiazole-containing diamines[11].



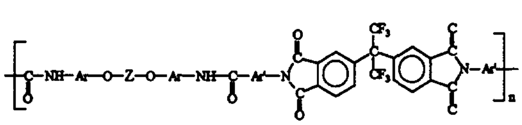
Scheme 3 Preparation of poly(imide-pyridazine-amide)s containing hexafluoroisopropylidene groups

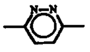
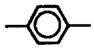
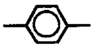
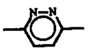
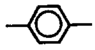
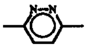
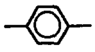
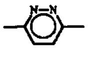
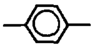
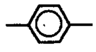
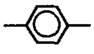
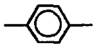
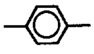


Scheme 4 Preparation of poly(imide-amide)s containing hexafluoroisopropylidene groups

Table 1 Properties of fluorinated poly(imide-pyridazine-amide)s and fluorinated poly(imide-amide)s

General Formula



Polymer	Z	Ar	Ar′	η_{inh} (dl g^{-1})	Dielectric constant at *RH* of 0%	30%	60%	80%	T_g (°C)	*IDT*[a] (°C)	Weight loss at 500°C (%)
III a				0.61	4.01	4.84	5.39	5.70	305	414	22.8
III b				0.44	3.88	4.84	5.77	6.46	264	416	13.9
III c				0.60	3.75	4.31	4.74	5.13	278	412	14.3
III d				0.43	3.95	4.69	5.16	5.46	258	415	13.4
IV a				1.18	3.35	3.86	4.26	4.51	300	449	11.8
IV b				0.71	3.41	3.92	4.23	4.53	261	450	8.1

[a] Initial decomposition temperature

All of the poly(imide-pyridazine-amide)s (III) have lower viscosities than the related poly(imide-amide)s (IV) (η_{inh}=0.7–1.1 dl g^{-1}), which may be due to the lower reactivity of the pyridazine-containing diamines when compared to the related aromatic diamines which contain no pyridazine rings.

The expected structures of the poly(imide-pyridazine-amide)s III were confirmed by i.r. spectroscopy. The strong bands appearing at 1780, 1720 and 720 cm^{-1} were assigned to the imide rings. These bands are also present in the spectra of the preformed imide monomers II. The amide groups in the polymer backbone were identified through the wide absorptions at 3370–3340 cm^{-1}, characteristic of NH, and the band at 1680 cm^{-1}, which is due to CO in the amide group.

All of these polymers gave transparent flexible films by casting solutions in NMP onto glass plates, followed by gradual heating to 300°C to remove the solvent. Even those polymers having the lower viscosities (IIIb and IIId) gave quite flexible films, which can be explained by the presence of the hexafluoroisopropylidene units and other flexible groups (such as ether) in the main chain. Free-standing films, having a thickness of 2–5 μm, have been prepared for use in recording the i.r. spectra, while somewhat thicker films (20–30 μm) have been produced for dielectric measurements.

The thermogravimetric analysis of these polymers in air shows that the fluorinated poly(imide-pyridazine-amide)s (III) begin to decompose in the range 412–416°C, while the related polymers without the pyridazine rings (IV) start to decompose at 449–450°C (*Table 1*). At 500°C, the weight losses for III are 13.4–22.8%, while that of IV are 8.1–11.8%. These data show that the compounds containing pyridazine rings (III) have a slightly lower thermal stability than do the related polymers without these units (IV). A possible explanation for this lower thermal stability is that early decomposition of the poly(imide-pyridazine-amide)s might take place, involving the elimination of molecular nitrogen. Previous work on poly(imide-pyridazine)s also showed a lower thermal stability of those materials, when compared to related polyimides prepared without any pyridazine groups[9]. The glass transition temperatures of III (determined by d.s.c.), are in the range 258–305°C, with those of IV being in the range 261–300°C (*Table 1*). The T_gs of the poly(imide-pyridazine-amide)s IIIa and IIIb, when compared to IVa and IVb, respectively, which have similar structures, are practically identical. A significant decrease in the T_gs of polymers IIIb and IVb, which contain *m*-substituted phenylene rings, can be noticed, when compared to polymers IIIa and IVa, which contain only *p*-structures (258–278°C, compared to 300–305°C). The polymer IIId, containing the largest amount of *m*-structure shows the lowest T_g, i.e. 258°C. In this series of polymers, the effect of the *m*-structure content on the decrease of T_g is very clearly observed. It can also be noticed that there is a large 'window' between the T_g and the decomposition temperature, which could be advantageous in the processing of these polymers.

The electrical insulating properties were evaluated on the basis of the dielectric constants, measured at different relative humidity (*RH*) levels[12]. The dielectric constants of the poly(imide-pyridazine-amide)s (III) (at $RH = 0\%$) are in the range 3.75–4.01, while that of the related poly(imide-amide)s (IV) are 3.35–3.41 (*Table 1*). These values are of the same order of magnitude as that of 'H film', a polyimide which is prepared from pyromellitic dianhydride and 4,4′-diaminodiphenylether, and which is one of the most common polyimides used as a dielectric in microelectronic applications[2], having a dielectric constant of 3.5. However, the polymers which contain pyridazine rings (III) have slightly increased dielectric constants when compared to the related polymers prepared without pyridazine groups (IV). Since the dielectric constant of a polymer is a function of its total polarizability[13], the present polymers which display higher dielectric constants should also have higher polarizabilities. The higher dielectric constants of the poly(imide-pyridazine-amide)s are attributed to the high polarizability of the pyridazine moieties which are present in the chain. With increasing relative humidity, an increase in the dielectric constant takes place and this is also somewhat higher than in the case of the polymers which do not contain any pyridazine groups. Thus, at a *RH* of 80% the dielectric constants of III are in the range 5.13–6.46, while those of IV are 4.51–4.53. The compared increases in the dielectric constants of these polymers *versus* relative humidity is illustrated in *Figure 1*. The larger increases in the dielectric constants of the poly(imide-pyridazine-amide)s with increasing relative humidity is attributed to the higher levels of moisture absorption, which is facilitated by hydrogen bonding of water molecules to the pyridazine moieties.

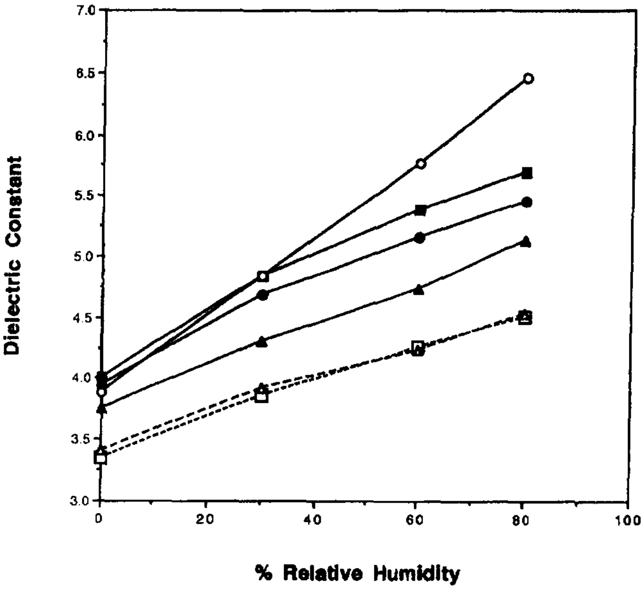


Figure 1 Dielectric constant *versus* relative humidity for the fluorinated poly(imide-pyridazine-amide)s and fluorinated poly(imide-amide)s: (■) IIIa; (○) IIIb; (▲) IIIc; (●) IIId; (□) IVa; (△) IVb

CONCLUSIONS

A series of novel fluorinated poly(imide-pyridazine-amide)s has been synthesized by the low temperature solution polycondensation of aromatic diamines containing preformed pyridazine rings with diacid chlorides which incorporate both imide and hexafluoroisopropylidene units. Due to the presence of the hexafluoroisopropylidene groups in the main chain, these polymers are readily soluble in NMP and other amide solvents, which is very convenient for their processing. Free-standing films, which are very thin and flexible, have been obtained by casting polymer solutions onto glass substrates. These polymers have low dielectric constants, which are sensitive to the relative humidity. They show a high thermal stability, with initial decomposition temperatures in the range 412–416°C, and glass transition temperatures which are in the range 258–305°C. These properties, associated with an easy processability, make these polymers potential candidates for practical applications in microelectronics and related industries.

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