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POLYISOPHTHALAMIDES WITH PENDANT 3,4,5,6-TETRACHLOROPHTHALIMIDE GROUPS

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ABSTRACT

New polyamides containing pendant chlorinated phthalimide groups have been synthesized by solution polycondensation of various aromatic diamines with 5-(3,4,5,6-tetrachlorophthalimide)isophthaloyl chloride. These polymers are soluble in such polar amidic solvents as *N*-methyl-2-pyrrolidinone and *N*,*N*-dimethylformamide and give transparent flexible films by casting from solutions. They show high thermal stability with a decomposition temperature above 400°C and no glass transition up to 350°C. They have low dielectric constants in the 3.6–4.0 range and good tensile properties.

INTRODUCTION

Aromatic polyamides are widely used as high-temperature-resistant polymers. Numerous polyamides containing different substituents on the aromatic rings have been synthesized and studied for high performance applications [1, 2]. The polyamides containing all *para*-phenylene rings are the most interesting polymers, but they are not soluble nor fusible, and therefore they are processed with great difficulty. A major parameter that contributes to insolubility is the intermolecular bonding energy developed through hydrogen bridges and through dipole–dipole interactions. Regular aromatic polyamides, obtained from symmetrical comonomers, develop a high degree of crystallinity, a factor that works against solubility and processability [3].

The introduction of a certain amount of *meta*-phenylene rings led to polymers with somewhat improved solubility. Thus, polyisophthalamides are soluble in highly polar solvents in the presence of inorganic salts [4].

Another attractive synthetic approach to improving the solubility and processability is the incorporation of bulky substituents such as pendant groups along the polymer backbone. If the pendant groups are carefully chosen, it is possible to promote solubility without sacrificing the thermal and mechanical properties to a great extent. Thus, thermally stable polyamides with pendant aromatic and heteroaromatic rings have been reported [5–9].

In the present work, polyisophthalamides with 3,4,5,6-tetrachlorophthalimide pendant groups have been prepared, and their properties have been evaluated with respect to their chemical structure. Our main goal was to develop new polymeric structures which combine the excellent thermooxidative stability of the polyimides and the processing ability of polyisophthalamides.

The polymers were synthesized by solution polycondensation of aromatic diamines containing various linkages, such as ether, sulfonyl, isopropylidene, or hexafluoroiso propylidene, with a diacid chloride incorporating a 3,4,5,6-tetrachlorophthalimide unit.

EXPERIMENTAL

Starting Materials

N-Methyl-2-pyrrolidinone (NMP) from Merck was dried over phosphorous pentoxide and distilled under reduced pressure. Thionyl chloride from Merck was freshly distilled. The 3,4,5,6-tetrachlorophthalic anhydride, 5-aminoisophthalic acid, pyridine (Py), *N,N*-dimethylformamide (DMF), and glacial acetic acid were purchased from Fluka and used as received. Aromatic diamines, **I**, such as 4,4′-diaminodiphenylether, bis(*p*-aminophenoxy)-1,4-benzene, bis(*p*-aminophenoxy)-1,3-benzene, bis(*p*-aminophenoxy)-4,4′-biphenyl, bis(*p*-aminophenoxy-phenyl)-2,2-propane, bis(*p*-aminophenoxy)-4,4′-diphenylsulfone, bis(*p*-aminophenyl)-2,2′-hexafluoropropane, and bis(3-methyl-4-amino-phenyl)-2,2-hexafluoropropane, from commercial sources, were used without further purifications.

Synthesis of the Monomers

Preparation of 5-(3,4,5,6-Tetrachlorophthalimide)isophthalic Acid (II′)

The dicarboxylic acid synthesis was carried out in a round-bottom flask equipped with a condenser, $CaCl_2$ drying tube, magnetic stirrer, and heating source. The concentration of reactants used in this synthesis was 8% solids (w/v) which allowed efficient mixing. Glacial acetic acid (600 mL) was placed in the flask and 28.6 g (0.1 mol) of 3,4,5,6-tetrachlorophthalic anhydride was added to the flask. 18.1 g (0.1 mol) of 5-aminoisophthalic acid was added to the flask at room temperature with rapid stirring. The reaction mixture was stirred at room temperature for 4 hours and then heated at reflux for 18 hours. The resulting white product was filtered hot and washed with water and dried (90.5% yield). Mp > 400°C (Scheme 1).

Analysis: Calculated for $C_{16}H_5NO_6Cl_4$: C, 42.76%; H, 1.11%; N, 3.12%; Cl, 31.6%. Found: C, 42.15%; H, 1.36%; N, 3.05%; Cl, 30.85%.

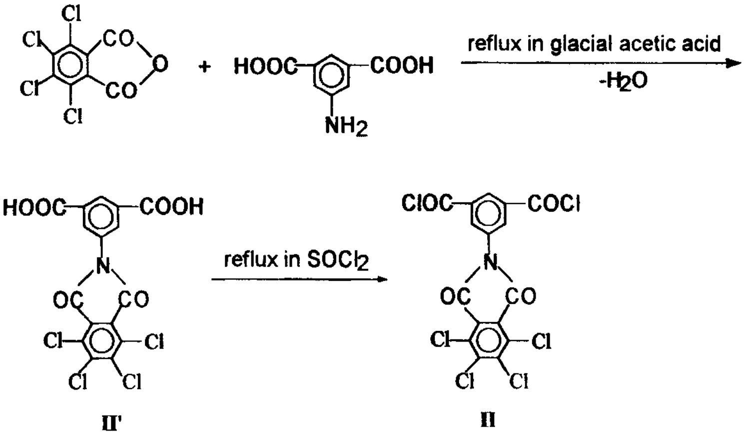
IR spectrum (KBr, cm^{-1}): 3070–2510 (—OH stretching); 1780 (imide carbonyl symmetric stretching); 1720 (imide carbonyl asymmetric stretching and carboxylic C=O); 1100 and 725 (imide ring).

Preparation of 5-(3,4,5,6-Tetrachlorophthalimide)isophthaloyl Chloride (II)

10 g of diacid, **II**′, was heated at reflux for 10 hours with 40 mL thionyl chloride and 1 drop of DMF as a catalyst. A white needle-like product crystallized during heating. It was cooled, filtered, washed with hexane, and dried (87.5% yield). Mp: 268–270°C (Scheme 1).

Analysis: Calculated for $C_{16}H_3NO_4Cl_6$: C, 39.50%; H, 0.62%; N, 2.88%; Cl, 43.41%. Found: C, 40.01%; H, 0.76%; N, 2.98%; Cl, 42.66%.

IR spectrum (KBr, cm^{-1}): 1780 (—COCl and imide carbonyl symmetric stretching); 1720 (imide carbonyl asymmetric stretching); 1100 and 720 (imide ring).



SCHEME 1. Preparation of diacid chloride **II**.

Synthesis of the Polymers

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 a 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 inlet and outlet were placed 1 g (0.005 mol) **Ia**, 35 mL NMP, and 0.4 mL Py, and the mixture was stirred until complete dissolution. The solution was cooled to −10°C, and 2.43 g (0.005 mol) of **II** was added with rapid stirring. The content of the flask was kept below 0°C for 15 minutes. 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 hours. Half of the resulting viscous solution was cast onto a glass plate, and after evaporating the solvent at 120, 160, 180, and 220°C for periods of 1 hour each, a flexible transparent film was obtained which was stripped off the plate by immersion in hot water for 2 hours. The film was used for different measurements. The other half of the polymer solution was diluted to about 4% by addition of more NMP, and the polymer was precipitated by pouring into water. The precipitated product was filtered, washed twice with ethanol under stirring, and dried under vacuum at 80°C for 1 hour.

Measurements

The inherent viscosities of the polymers were determined in NMP at 20°C at a concentration of 0.5 g/dL by using an Ubbelohde viscometer.

Infrared spectra were recorded on a Specord M-80 Spectrophotometer using KBr pellets or polymer films with a thickness of 2–5 μm.

The glass transition temperatures (T_gs) of the precipitated polymers were determined with a Seiko differential scanning calorimeter DSC 200 C using a heating rate of 10°C/min.

The thermooxidative stability was investigated using a Seiko TGA/DTA 220 thermobalance operating at a heating rate of 20°C/min in air. The data were collected and analyzed by using the Seiko SSS 520 data system. The initial decomposition temperature (IDT) is characterized as the temperature at which the samples achieve a 5% weight loss. The temperature of 10% weight loss (T_{10}) and the weight loss at 500°C were also recorded.

The dielectric constants were measured using the previously described fluid displacement method [10]. 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.

Uniaxial stress–strain curves were recorded at room temperature with a crosshead speed of 9.0 mm/min using a tensile testing machine built in our laboratory. The dumbbell-type specimen was 10 mm wide at the two ends and 4.5 mm wide and 10 mm long at the neck.

^{1}H-NMR spectra were recorded on a Jeol C-60 MHz Spectrometer for solution in dimethylsulfoxide-d_6 using tetramethylsilane as internal standard.

Melting points were measured on a Melt-Temp II (Laboratory Devices) apparatus without correction.

RESULTS AND DISCUSSION

Polycondensation of equimolar amounts of aromatic diamines (**I**) and diacid chloride (**II**) in NMP at low temperature yielded viscous solutions of polyisophthalamides containing pendant 3,4,5,6-tetrachlorophthalimide groups (**III**) according to Scheme 2.

The structure of the polymers was identified by infrared and ^{1}H-NMR spectra and elemental analysis.

In infrared spectra the absorptions at 1780 and 1720 cm^{-1} are commonly attributed to the symmetrical and asymmetrical stretching vibrations of carbonyl groups of imide; the absorptions at 1100 and 720 cm^{-1} are possibly due to imide ring deformations. The wide bands which appeared at 3450 cm^{-1} were attributed to the NH stretching vibration in the amide group. Characteristic absorptions appeared at 1680–1670 cm^{-1} due to the carbonyl stretching vibration (amide I) and at 1530–1520 cm^{-1} due to NH deformational vibration (amide II). Polymers **IIIa-f** showed IR bands at 1260 cm^{-1} due to the ether linkages. Polymers **IIIf** and **IIIg** exhibited absorption peaks at 1320 and 1140 cm^{-1} due to the SO_2 groups, and polymers **IIIh** and **IIIk** exhibited IR bands at 1180 and 1210 cm^{-1} due to the hexafluoroisopropylidene groups. Figure 1 shows the IR spectrum of polymer **IIIh**.

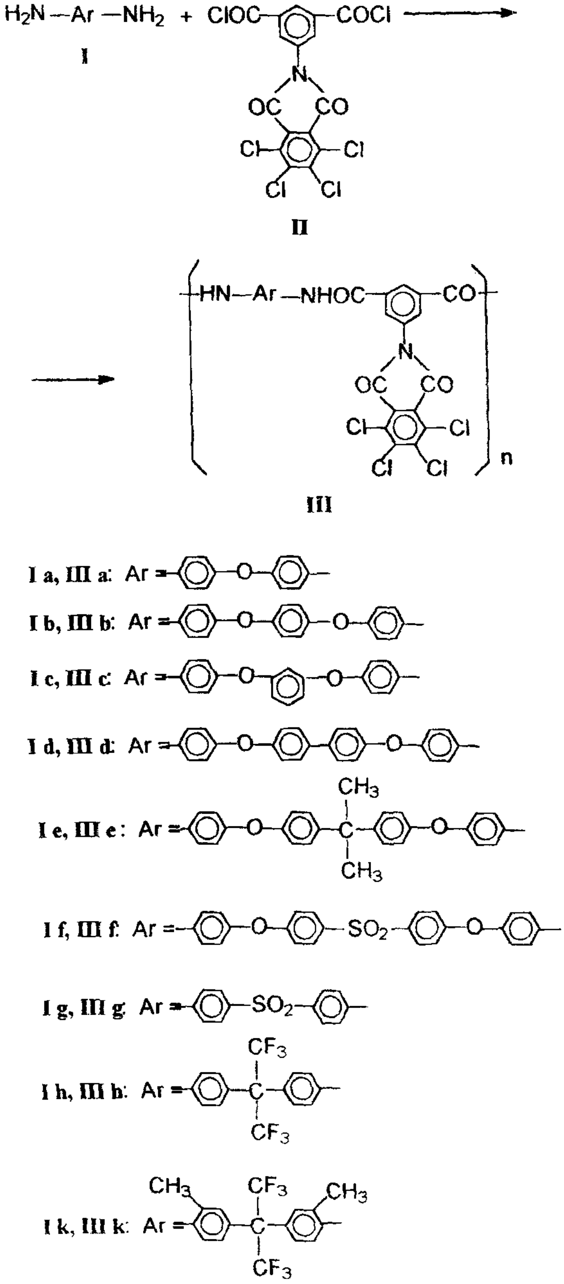
The ^{1}H-NMR spectrum of polyisophthalamide (**IIIa**) in dimethylsulfoxide-d_6 solution shows peaks at 10.87 ppm (NHCO), 8.57–8.09 ppm (aromatic H *ortho* to C=O), and 7.47–7.35 ppm (other aromatic) (Fig. 2).

Elemental analysis data for C, H, N, and Cl of these polymers are in good agreement with the calculated values.

All these polymers were readily soluble in such aprotic solvents as NMP and DMF. Except for polymer **IIIg**, they were soluble even in less polar solvents like pyridine. This behavior is in agreement with the fact that the presence of voluminous imide side rings introduces a factor of asymmetry and sterical hindrance that prevents dense packing and enhances the solubility. Polymers like **IIIe**, **IIIh**, and **IIIk** were partially soluble even in tetrahydrofuran (THF), probably due to the presence of isopropylidene units (Table 1). Thus, the present polymers containing pendant tetrachlorophthalimide groups have better solubility in organic solvents compared to polyisophthalamides which are only soluble in polar amidic solvents [4].

The inherent viscosities of polymers **III** were in the 0.39–0.88 dL/g range (Table 2).

Chemical stability of polymer films was evaluated by examining their aspect upon immersion in acidic or basic media for periods up to 1 month. Free-standing films were kept in glacial acetic acid, in 10% HCl, or in 10% NaOH solution. After 1 month the films which were kept in acidic media were flexible and apparently unchanged. Indeed, IR spectra of the acid-treated films were identical to those of the initial, untreated films. Also, UV spectra of the acidic solution in which the polymer film was immersed didn't exhibit any absorption which might be attributed to some products of hydrolysis. When immersed in 10% NaOH solution for 1 month, the films became brittle but they were still films. At the same time, a sample film prepared from the polyimide "H" (synthesized by polycondensation of pyromellitic dianhydride with 4,4′-diaminodiphenylether) became a gel after immersion for only 3 days in 10% NaOH solution. Therefore it can be stated that the present polymer films have a good stability toward acidic media, but they lose



SCHEME 2. Preparation of the polymers **III**.

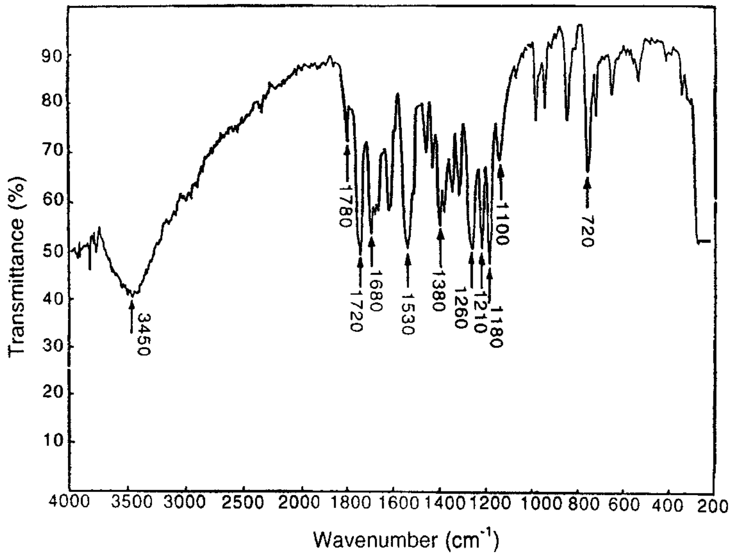


FIG. 1. IR spectrum of polymer **IIIh**.

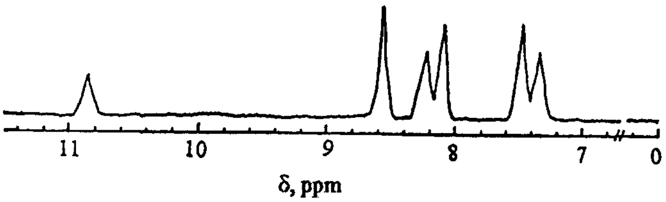


FIG. 2. ^{1}H-NMR spectrum of polymer **IIIa**.

TABLE 1. Solubility of Polymers **III**

	Solvent[a]				
Polymer	NMP	DMF	Py	THF	Chloroform
IIIa	+	+	+	−	−
IIIb	+	+	+	−	−
IIIc	+	+	+	−	−
IIId	+	+	+	−	−
IIIe	+	+	+	±	−
IIIf	+	+	+	−	−
IIIg	+	+	±	−	−
IIIh	+	+	+	±	−
IIIk	+	+	+	±	−

[a] + soluble, ± partially soluble or swollen, − insoluble.

TABLE 2. Properties of Polymers III

Polymer	η_{inh},[a] dL/g	IDT,[b] °C	Temperature of 10% weight loss, °C	%Weight loss at 500°C
IIIa	0.53	415	465	19
IIIb	0.78	400	448	21
IIIc	0.84	405	452	23
IIId	0.88	420	467	19
IIIe	0.69	400	430	27
IIIf	0.72	442	472	19
IIIg	0.39	460	495	18
IIIh	0.51	444	494	19
IIIk	0.45	415	460	21

[a] Determinated at 20°C in NMP at a concentration of 0.5g/100 mL solution.

[b] Initial decomposition temperature.

their integrity in basic media. This behavior is similar to that of the aromatic polyimides and poly(amide-imide)s, and it is explained by the hydrolysis of the imide rings in basic media [11].

The thermal stability of the polymers was evaluated by thermogravimetric analysis (TGA). Some characteristic TG curves are shown in Fig. 3.

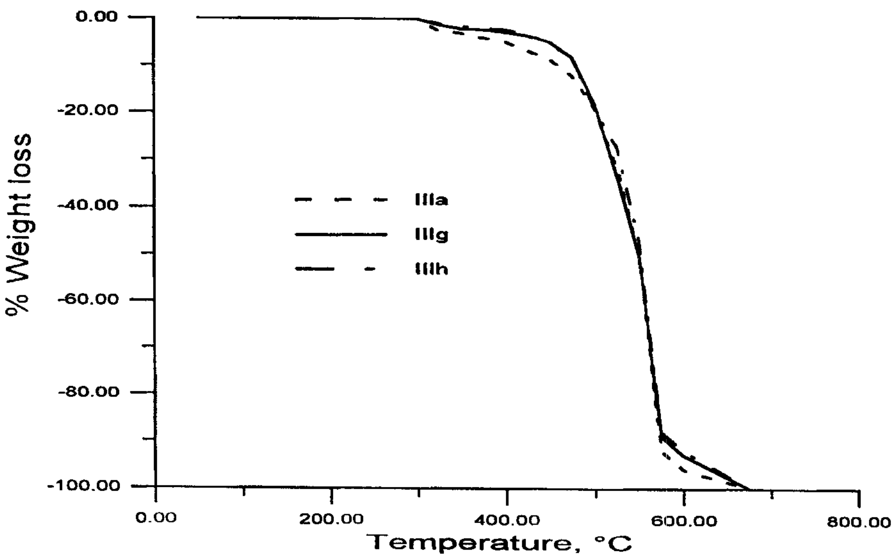


FIG. 3. TG curves of polymers **IIIa, IIIg**, and **IIIh**.

All the polymers exhibited high thermooxidative stability with no significant weight loss up to 400°C. They showed 10% weight loss in the 430–495°C range. Polymers **IIIf**, **IIIg**, and **IIIh**, containing sulfone or hexafluoroisopropylidene groups which begin to decompose at 442–460°C, seem to be more thermostable than the other polymers whose initial decomposition temperature is in the 400–420°C range. This behavior could be explained by the superior resistance of sulfone and hexafluoroisopropylidene units to thermal degradation compared to ether groups. Polymer **IIIk** containing hexafluoroisopropylidene groups and methyl substituents on the phenylene rings begins to decompose earlier (at 415°C) than the related polymer **IIIh** without methyl substituents, probably due to the fact that methyl groups are more sensitive to oxidative degradation. The total weight loss at 500°C is in the 18–27% range. Polymer **IIIe** containing isopropylidene linkages shows the highest weight loss (27%) at 500°C.

Comparison of these polymers with previously synthesized polyisophthalamides with pendant phthalimide groups but not containing any chlorine substituents shows that their thermooxidative stabilities are very similar. Some of the present polymers show slightly superior thermooxidative stability (temperature of 10% weight loss of polymers **IIIa** and **IIIg** = 465 and 495°C, respectively) when compared to the reported polyisophthalamides prepared by the reaction of isophthaloyl chloride with the same diamines used by us (temperature of 10% weight loss = 460 and 463°C, respectively) [6].

Polyisophthalamides with pendant 3,4,5,6-tetrachlorophthalimide groups did not melt nor soften (visually) under 350°C. Likewise, they did not show any fusion peak nor clear T_g inflections in DSC curves up to 350°C.

When the polymer films were heated at 220°C for a long time (4–6 hours) in air, they became completely insoluble. That could be due to some arrangement into a three-dimensional structure that resists solvation. Such a property can be of significant practical advantage when the polymer films are required to be highly stable to chemical reagents.

The tensile properties of some polymer films are summarized in Table 3.

The films have tensile strength in the 27–64 MPa range, elongation to break between 13 and 23%, and initial modulus in the 260–520 MPa range. The measured

TABLE 3. Dielectric Constants and Tensile Properties of Polymers **IIIa–f**

Polymer	Dielectric constant	Tensile strength, MPa	Elongation to break, %	Initial modulus, MPa
IIIa	4.03	27	23	260
IIIb	3.96	64	21	520
IIIc	3.72	32	13	320
IIId	3.91	42	17	410
IIIe	3.63	37	14	370
IIIf	4.06	35	16	290

values of the mechanical properties are comparable to those of other related aromatic polyamides [9].

Electroinsulating properties of the present polymers have been evaluated from the dielectric constant values. All these polymers have low dielectric constants, in the 3.6–4 range. However, these values are slightly higher than that (3.5) of the polyimide film (Kapton) obtained from pyromellitic dianhydride and 4,4′-diaminodiphenylether, which is one of the most used dielectrics in high performance applications. The polymers containing 3,4,5,6-tetrachlorophthalimide groups have slightly increased dielectric constants when compared with related polymers containing nonchlorinated units [9]. Since the dielectric constant is a function of the total polarizability of the molecule [12], the polymers which display higher dielectric constants should also have higher polarizabilities. The higher dielectric constants of the present polymers are determined by high polarizability of the 3,4,5,6-tetrachlorophthalimide groups which are present in their macromolecular chains.

CONCLUSIONS

By introducing tetrachlorophthalimide groups pendant to the polyisophthalamide chain, a significant increase of the polymer solubility was achieved, thus allowing easy processing into films or coatings by casting from polymer solution. After thermal treatment above 220°C, the polymer films become completely insoluble and stable to chemical reagents. These polymers are highly thermostable and have good mechanical and electroinsulating properties, thus being potential candidates for application in microelectronics and related industries.

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