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### Synthesis and Properties of New Polyphenylquinoxaline-imide-amides

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## **SYNTHESIS AND PROPERTIES OF NEW POLYPHENYLQUINOXALINE-IMIDE-AMIDES**

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## ABSTRACT

New thermostable polymers containing imide and phenylquinoxaline units have been prepared by solution polycondensation of diaminophenylquinoxaline coupled by ether, methylene, or sulfone linkages with diacid chlorides containing preformed imide rings. Solubility, thermal stability, and electroinsulating properties of these compounds are discussed and compared with those of related heterocyclic polymers previously reported.

## INTRODUCTION

Fully aromatic polyimides exhibiting outstanding stability at high temperature and good electrical insulating properties are used extensively as high performance materials [1]. However, their insolubility in the final cyclized form limits processability [2]; thus, research is being undertaken in order to find new structures with improved processing properties. To this aim, polyphenylquinoxalines show remarkable solubility in organic solvents along with film-forming properties and good thermal stability [3]. Therefore, synthesis of polymers containing both imide and phenylquinoxaline units is a possible way to obtain easily processable, highly thermostable macromolecules. We have prepared polyphenylquinoxaline-imide-amides by polycondensation of aromatic diamines containing preformed polyphenylquinoxaline rings and different flexible coupling groups such as ether, methylene, or sulfone with diacid chlorides with preformed imide units.

## EXPERIMENTAL

### Reagents

Dimethylformamide (DMF) and *N*-methylpyrrolidone (NMP) were dried over sodium hydroxide pellets and distilled over phosphorus pentoxide under reduced pressure before use. Symmetrical diaminophenylquinoxalines Ia–Ic were synthesized from 4-aminobenzil and the appropriate tetraamine as previously described [4] according to the following example. In a 200-mL three-necked flask provided with mechanical stirrer, N<sub>2</sub> inlet and outlet, and a reflux condenser, 0.004 mol 4-aminobenzil, 0.002 mol 3,3',4,4'-tetraaminodiphenylether (or tetraaminodiphenylmethane or tetraaminodiphenylsulfone, respectively), and 100-mL ethyl alcohol were added and heated at reflux for 12–14 hours. At the beginning there was a clear solution, but after 2–3 hours of reflux a white product precipitated. It became yellowish with further heating.

The precipitate was filtered, washed with ethanol, and dried. Finally, it was purified by recrystallization from a benzene:petroleum ether mixture (1:1). Melting points: Ia, 247–248°C; Ib, 222–224°C; and Ic, 315–317°C. In a similar procedure, the unsymmetrical diaminophenylquinoxaline I' (mp 173–175°C) was synthesized from 4-aminobenzil and 3,4,4'-triaminodiphenylether [4]. Bis-acid chlorides II were obtained upon treating the adducts of appropriate diamines and trimellitic anhy-

dride with thionyl chloride [5]. Corresponding treatment of the adducts of *m*- or *p*-aminobenzoic acid yielded monomers **II'** [6].

### Polymerizations

A three-necked flask equipped with mechanical stirrer and N<sub>2</sub> inlet and outlet was charged with 2.0 mmol diamine **I** or **I'** and 25 mL NMP. The mixture was stirred under nitrogen until complete dissolution occurred. Then the solution was cooled to -10°C, and 2.0 mmol diacid chloride **II** or **II'** was added with rapid stirring. The reaction temperature was maintained below -10°C for 15 minutes, then the temperature was allowed to rise to 20°C in the following 15 minutes and the stirring was continued at this temperature for 2 hours. The viscous yellow solution was neutralized with a few drops of pyridine. Half of this solution was cast onto a glass plate (size 200 × 200 mm), and after evaporating the solvent and drying in an oven at 100°C for 30 minutes, 150°C for 2 hours, and 200°C for 1 hour, a flexible transparent film was obtained. The other half of the solution was poured into water under rapid stirring. The yellow product which precipitated was filtered, washed three times each with 100 mL water, then with 100 mL acetone, and dried in an oven at 150°C for 24 hours. The films were used to measure the electrical properties, and the precipitates were used for all other investigations.

The concentration of diamine monomer varied between 4 and 12% according to the solubility of the polycondensate in the reaction medium. Higher concentrations (i.e., 10–12%) were used in the case of diamines **Ia**, **Ic**, and **I'**. Lower concentrations (4–5%) were used in the case of diamine **Ib** in order to avoid gelation of the reaction mixture.

### Measurements

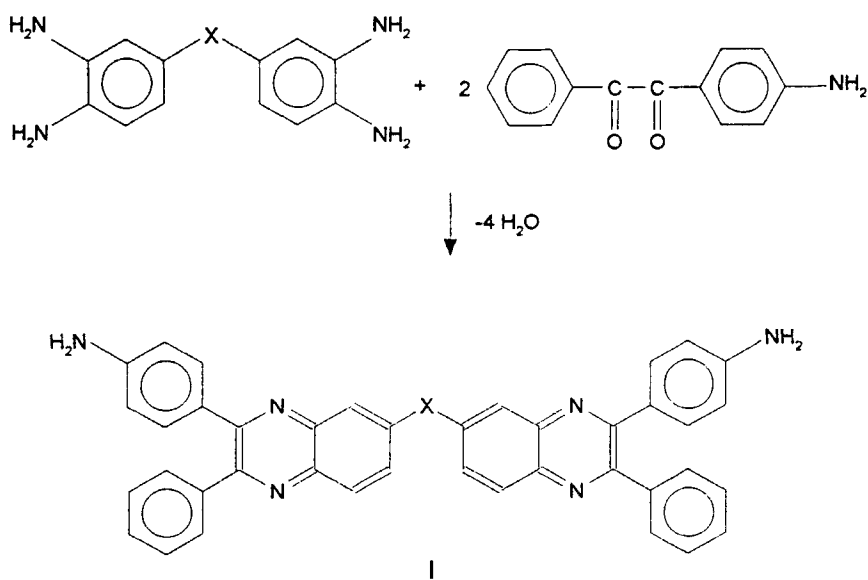
The inherent viscosity of the polymers was determined in NMP at 20°C at a concentration of 0.5 g polymer/100 mL solution. Infrared spectra of the polymer films were obtained with a Perkin-Elmer 1760X Fourier transform infrared (FTIR) spectrometer at 4 cm<sup>-1</sup> resolution and 25 scans. Glass transition temperatures (*T<sub>g</sub>*) of precipitated polymers were determined with a Seiko differential scanning calorimeter DSC 220C. Thermal stability was investigated using a Seiko TG/DTA 220 thermobalance. Measurements were made in both instruments in air with a heating rate of 10°C/min.

The dielectric constants were measured using the previously described fluid displacement method [9]. The capacitance of the film was measured using circular gold electrodes (1 in. diameter) mounted in a brass dielectric cell held at a constant temperature (25°C) and a GenRad Precision LC Digibridge (Model 1688) at 10 kHz. Relative humidity was measured by a General Eastman dew point Hygrometer (System 1100DP).

## RESULTS AND DISCUSSION

### Synthesis of Monomers

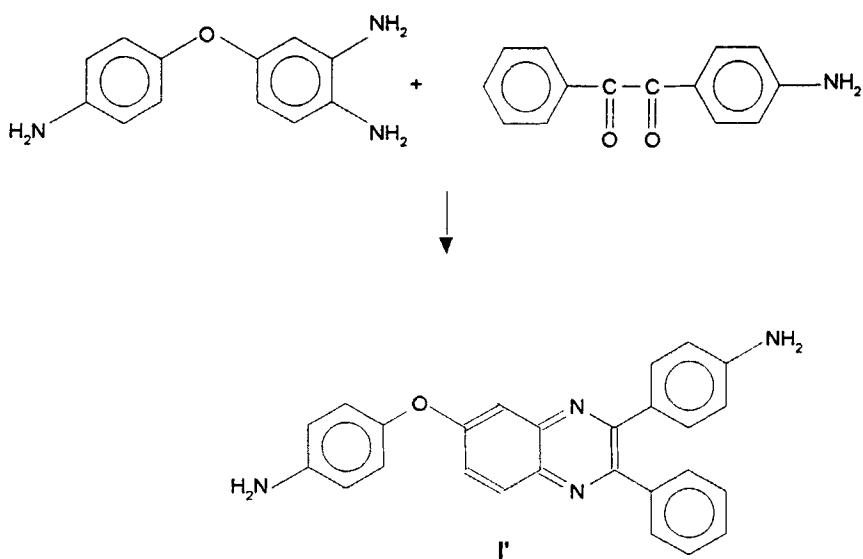
Symmetrical diaminophenylquinoxalines, **Ia**–**c**, were readily accessible by the reaction of 4-aminobenzil with aromatic tetraamines, i.e., 3,3',4,4'-tetraaminodiphenylether, 3,3',4,4'-tetraaminodiphenylmethane, and 3,3',4,4'-tetraaminodiphenylsulfone, respectively, according to the generic reaction shown in Eq. (1).



where: a) X = O; b) X = CH<sub>2</sub>; and c) X = SO<sub>2</sub>

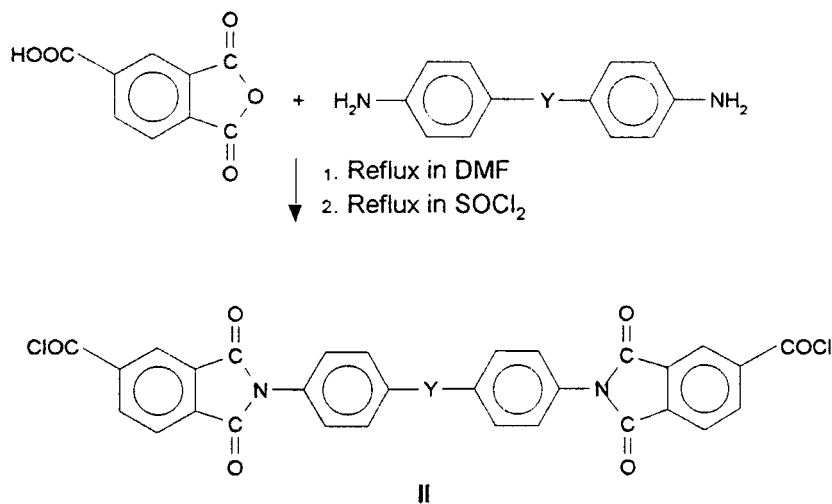
(1)

By replacing the tetramine with 3,4,4'-triaminodiphenylether, an unsymmetrical diaminophenylquinoxaline I' was formed as shown in Eq. (2). Two regioisomers might be formed in this reaction. However, no attempt was made to isolate them in pure form. Therefore, even if in the reactions only one isomer was depicted, i.e., I'c, as a matter of fact a mixture of isomers was employed.



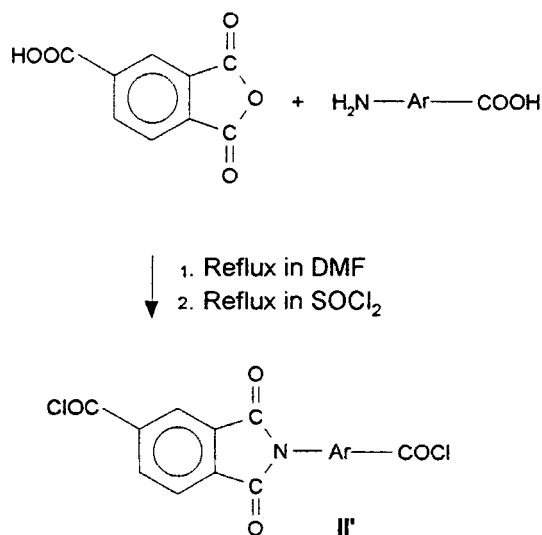
(2)

Reaction of trimellitic anhydride with either 4,4'-diaminodiphenylether or 4,4'-diaminodiphenylmethane in DMF could be controlled to produce dicarboxylic acid adducts. Treatment of these adducts with thionyl chloride at reflux [5] formed symmetrical diacid chlorides **IIa** and **IIb** (Eq. 3):



where: a) Y = O; and b) Y = CH<sub>2</sub> (3)

Unsymmetrical diacid chlorides **II'a** and **II'b** (Eq. 4) were synthesized similarly to diacid chlorides **II** by reacting thionyl chloride and the diacids obtained from trimellitic anhydrides and *p*- or *m*-aminobenzoic acid.



where: a) Ar = *p*-C<sub>6</sub>H<sub>4</sub>; and b) Ar = *m*-C<sub>6</sub>H<sub>4</sub> (4)

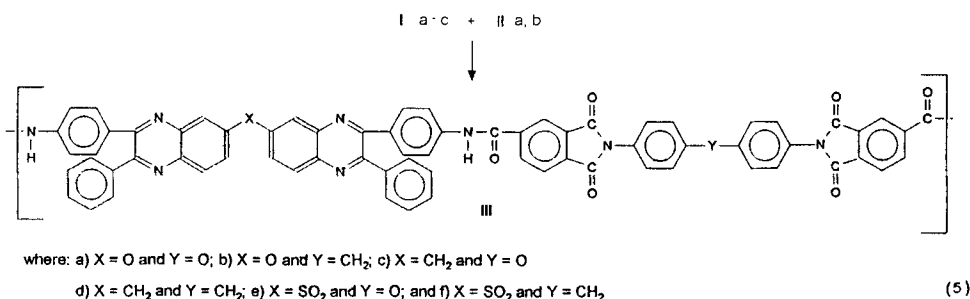
## Synthesis of Polymers

Low temperature solution polymerization of equimolar amounts of diamino-phenylquinoxaline and diacid chloride in the presence of pyridine yielded high molecular weight materials [7, 8]. All the polyphenylquinoxaline-imide-amides synthesized as shown above are soluble in polar aprotic solvents, such as NMP and dimethylacetamide (DMA) up to a concentration of 30–35%. The improved solubility of these polymers as compared to that of related polyimide-amides obtained by the reaction of the same diacid chlorides with simple aromatic diamines [10] can be explained by the presence of phenylquinoxaline rings. Since the phenylquinoxaline units are voluminous, the packing of macromolecular chains in tight structures due to hydrogen bonding through amide groups is disturbed. Consequently, the solvent molecules can penetrate easily to solubilize the chains. However, the structure of preformed monomers plays an important role as regards the properties of polycondensates.

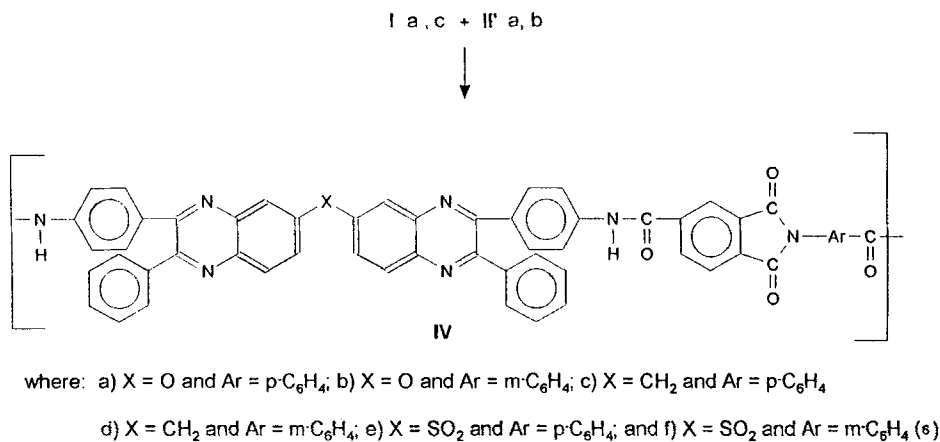
Polyphenylquinoxalines-imide-amides **III** were prepared from monomers **I** and **II** (Eq. 5) (see page 795). Polymers **IIIa** and **IIIb** obtained from diamine **Ia** exhibited the highest inherent viscosity, and flexible films were obtained by casting the polymers from the reaction medium (Table 1). Polyphenylquinoxaline-imide-amides **IIIc** and **IIId** resulting from diamine **Ib** and symmetrical diacid chlorides **IIa** and **IIb** gave brittle films, while polymers **IIIe** and **IIIf**, obtained from diamine **Ic**, had the lowest viscosity. Films prepared from these materials were very brittle.

TABLE 1. Inherent Viscosity and Film-Forming Properties of Polyphenylquinoxaline-imide-amides

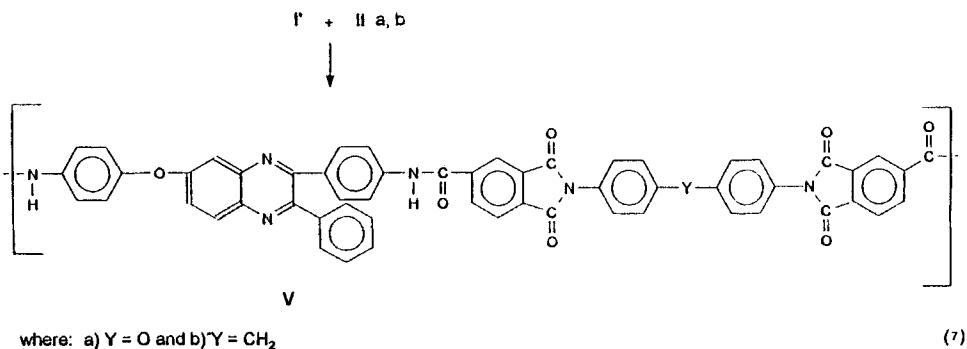
Polymer	Diamine	Diacid chloride	$\eta_{inh}$	Film properties
<b>IIIa</b>	<b>Ia</b>	<b>IIa</b>	0.80	Flexible
<b>IIIb</b>	<b>Ia</b>	<b>IIb</b>	0.80	Flexible
<b>IIIc</b>	<b>Ib</b>	<b>IIa</b>	0.35	Brittle
<b>IIId</b>	<b>Ib</b>	<b>IIb</b>	0.35	Brittle
<b>IIIe</b>	<b>Ic</b>	<b>IIa</b>	0.20	Very brittle
<b>IIIf</b>	<b>Ic</b>	<b>IIb</b>	0.20	Very brittle
<b>IVa</b>	<b>Ia</b>	<b>II'a</b>	0.75	Flexible
<b>IVb</b>	<b>Ia</b>	<b>II'b</b>	0.70	Flexible
<b>IVc</b>	<b>Ib</b>	<b>II'a</b>	—	Gel
<b>IVd</b>	<b>Ib</b>	<b>II'b</b>	—	Gel
<b>IVe</b>	<b>Ic</b>	<b>II'a</b>	0.20	Very brittle
<b>IVf</b>	<b>Ic</b>	<b>II'b</b>	0.25	Very brittle
<b>Va</b>	<b>I'</b>	<b>II'a</b>	0.55	Flexible
<b>Vb</b>	<b>I'</b>	<b>II'b</b>	0.55	Flexible
<b>VIa</b>	<b>I'</b>	<b>II'a</b>	0.20	Very brittle
<b>VIb</b>	<b>I'</b>	<b>II'b</b>	0.20	Very brittle



Soluble polymers IVa-b (Eq.6) were obtained from diamine Ia and unsymmetrical diacid chlorides II'a-b (Table 1). However, the attempted polymerization of diamine Ib with these diacid chlorides produced gels IVc and IVd; no further effort was made to characterize these materials. Only low molecular weight oligomers could be isolated when Ic was employed as a comonomer.



The unsymmetrical diamine, I', yielded suitable polymers Va-b when treated with symmetrical diacid chlorides IIa-b (Eq. 7), but only oligomers, VIa-b, were isolated when both unsymmetrical monomers were used.





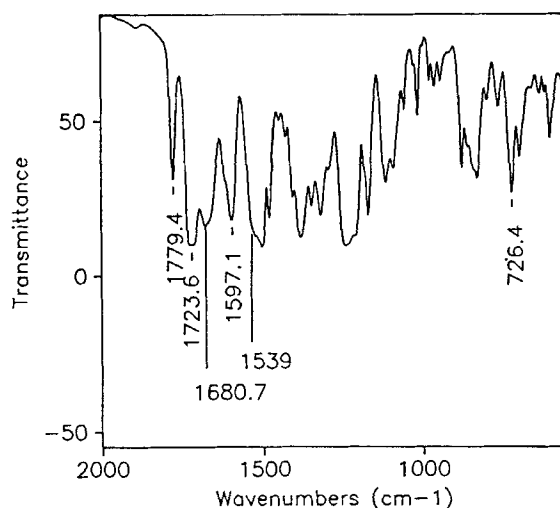


FIG. 1. FTIR spectrum of polyphenylquinoxaline-imide-amide **IIIa**.

The expected structures of polyphenylquinoxaline-imide-amide were confirmed by FTIR data as follows. The strong bands appearing at 1780–1770, 1720–1710, and 730–720  $\text{cm}^{-1}$  were assigned to the imide ring. These bands are also present in preformed imide monomers. The amide groups from the polymer backbone were identified through the N–H stretching vibration from 3350  $\text{cm}^{-1}$ , the amide I absorption from 1670–1660  $\text{cm}^{-1}$ , and the amide II absorption around 1540  $\text{cm}^{-1}$ . The FTIR spectrum of polymer **IIIa** illustrates these features (Fig. 1).

Inherent viscosities of at least 0.5 dL/g were required to cast flexible films; the brittle films produced by materials with viscosities of 0.35 or less indicate that molecular weights high enough to convey satisfactory mechanical properties have not been achieved (Table 1). Symmetrical diacid chlorides are required to produce high molecular weight materials using low temperature solution polymerization techniques.

All film-forming polymers are stable in air up to  $\sim 400^\circ\text{C}$ , their initial decomposition temperature being in the 400–450 $^\circ\text{C}$  range (Table 2). At 500 $^\circ\text{C}$  the total

TABLE 2. Thermal Properties of Polyphenylquinoxaline-imide-amides

Polymer	Initial decomposition temperature, $^\circ\text{C}$	Weight loss at 500 $^\circ\text{C}$ , %	$T_g$ , $^\circ\text{C}$
<b>IIIa</b>	425	10	297
<b>IIIb</b>	430	7	281
<b>IVa</b>	450	10	292
<b>IVb</b>	435	10	280
<b>Va</b>	400	12	245
<b>Vb</b>	400	16	260

weight loss was in the range of 7 to 16%. Polymers **IIIa**, **IIIb**, **IVa**, and **IVb**, prepared from symmetrical diamine **Ia**, showed higher thermal stability than did polymers **Va** and **Vb** obtained from nonsymmetrical diamine **I'**. The thermal behavior of these materials is quite similar to that of related polyphenylquinoxaline-imide-amides synthesized previously [11] from the same diacid chlorides, and to that of aromatic diamines with more extended phenylquinoxaline residues.

Glass transition temperatures ( $T_g$ ) of the present polyphenylquinoxaline-imide-amides, measured from both DSC and DTA curves, are in the range of 245 to 300°C (Fig. 2). Interestingly, polymers obtained from an unsymmetrical diamine, e.g., **Va** and **Vb**, exhibit lower  $T_g$ s than those prepared from symmetrical diamine **Ia**, e.g., polymers **IIIa**, **IIIb**, and **IVb** (Table 2). The large temperature range between  $T_g$  and the decomposition temperature makes these polyphenylquinoxaline-imide-amides attractive for processing.

Electrical insulating properties were evaluated on the basis of the value of dielectric constant at different relative humidity (RH) values [9]. The dielectric constant of the films at 0% RH is in the 3.21 to 3.67 range. Since these values are close to the dielectric constant of the polyimide film (H film) prepared from pyromellitic dianhydride and 4,4'-diaminodiphenyl ether [12] and from Ultem type polyimides, e.g., Ultem 1000 (dielectric constant = 3.15) [1], it follows that the introduction of phenylquinoxaline units into the main chain does not significantly affect the electric properties. The variation of the dielectric constant with RH is shown in Fig. 3. From the plotted values, one can observe that polymer **Va**, which contains unsymmetrical fragment derived from diamine **I'**, has the highest dielectric constant. Moreover, it is the most sensitive to the relative humidity. Symmetrical

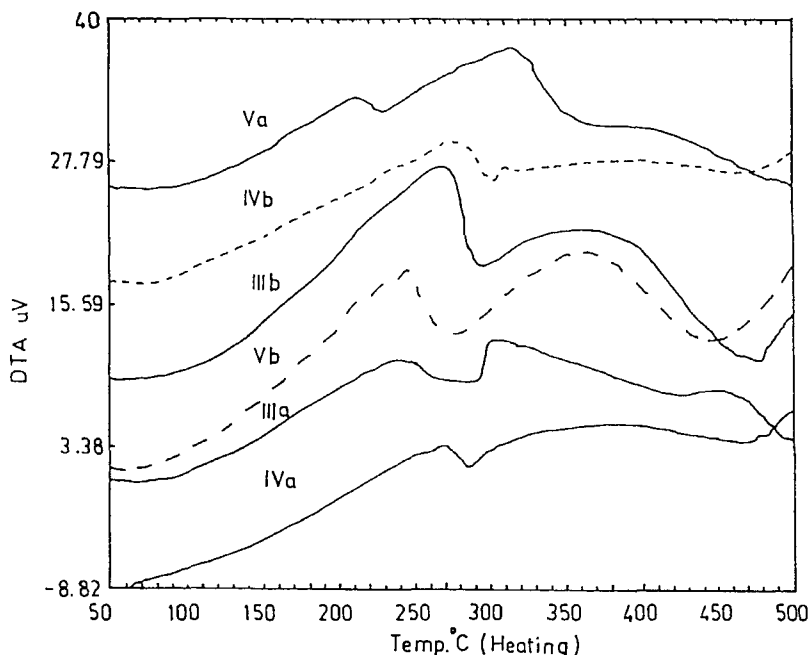


FIG. 2. DTA curves of polyphenylquinoxaline-imide-amide.

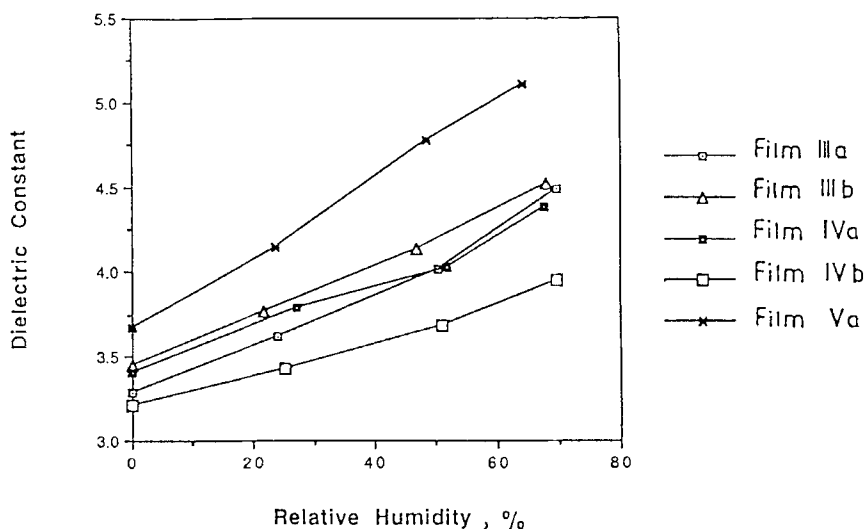


FIG. 3. Dielectric constant of polyphenylquinoxaline-imide-amides versus relative humidity.

polyphenylquinoxaline-imide-amides **III** and **IV** exhibit lower dielectric constants at comparable RH values.

## CONCLUSIONS

New symmetrical and unsymmetrical polyphenylquinoxaline-imide-amide structures have been synthesized by solution polycondensation of diaminophenylquinoxalines with diacid chlorides containing preformed imide rings. These polymers are soluble in polar aprotic solvents, and some of them can be cast as flexible films with good electrical insulating properties. They decompose over 400°C and have a glass transition in the 245 to 300°C range. Symmetrical structures exhibit better thermal stability, higher  $T_g$ s, and lower dielectric constants.

## ACKNOWLEDGMENTS

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