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THERMOSTABLE POLYMERS CONTAINING PHENYLQUINOXALINE AND OTHER HETEROCYCLIC UNITS

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ABSTRACT

Thermostable heterocyclic polymers containing phenyl-substituted quinoxaline and both amide and imide units have been synthesized by low-temperature solution polycondensation of diaminophenylquinoxalines with diacid chlorides of certain aromatic acids containing preformed imide rings. Also, copolymers have been obtained in which a mixture of diaminophenylquinoxaline and diaminooxadiazole or diaminobenzimidazole was used in the reaction with the same diacid chlorides. The thermal stability and the electrical insulating properties of these products are discussed and compared with related heterocyclic polymers.

INTRODUCTION

In the field of heterocyclic thermostable polymers it is known that fully aromatic and heteroaromatic structures lead to very good thermal stability, but at the same time these polymers are completely insoluble and infusible, which causes great processing difficulties. This is why certain thermostable polymers, such as polyimides that are presently in production, are made by a two-stage process: in the first step a soluble linear prepolymer is obtained that can be processed into films, fibers, or other thin-layer articles and then, in the second step, these materials undergo a special treatment that determines the polyheterocyclization along the macromolecular chain to give the final highly thermostable structure [1]. But during the polyheterocyclization, low molecular weight volatile products are evolved, so that the properties of the final articles cannot attain the full advantage from their chemical structures. Many attempts have been made to improve the processing properties of heterocyclic thermostable polymers, particularly their solubility and fusibility. Among thermostable polymers widely studied in the last two decades, special attention has been paid to polyquinoxalines which showed an excellent potential for high-temperature applications along with very good storageability at ambient temperature. Moreover, phenyl-substituted quinoxaline polymers have good solubility in organic solvents, which facilitates their detailed study and processing into useful materials [2].

It has been established that among heterocyclic structures, poly-1,3,4-oxadiazoles had the best thermal stability in oxidative atmospheres owing to the nature of the oxadiazole ring [3]. Also, polybenzimidazole-type polymers are well known for their excellent stability at high temperature along with good mechanical and electrical properties [4]. A combination of some of these structures, phenylquinoxaline, imide, oxadiazole, and benzimidazole, into one macromolecular chain was expected to provide high-performance physical and thermal characteristics as well as readily processable polymers. At the same time, flexible groups such as amide, introduced between aromatic and heteroaromatic rings, were meant to improve the solubility even more and to generate better mechanical properties in the final materials.

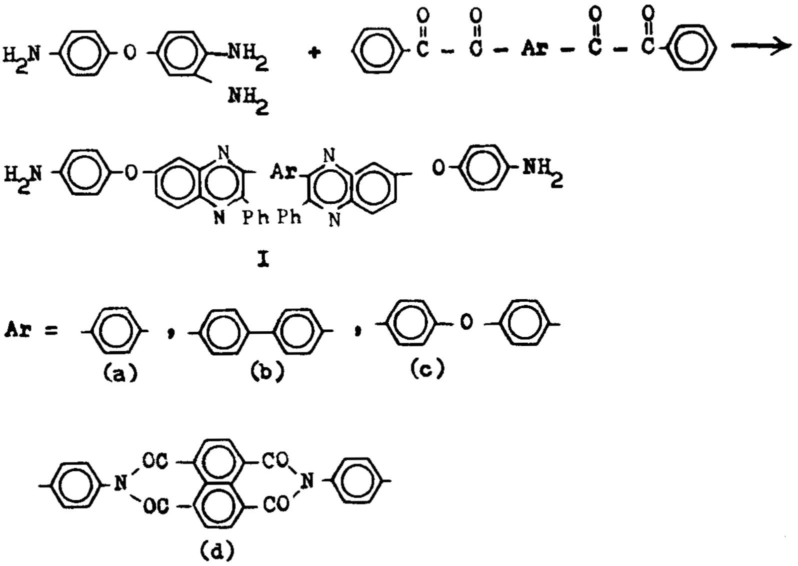
Thus, polyphenylquinoxaline-imide-amides, *co*-polyphenylquinoxaline-oxadiazole-imide-amides, and *co*-polyphenylquinoxaline-benzimidazole-imide-amides have been synthesized by polycondensation reaction of monomers which incorporates each of these preformed heterocycles, introducing flexible amide groups between aromatic and heteroaromatic rings.

EXPERIMENTAL

Synthesis of the Monomers

Heterocyclic Diamines

The *diaminophenylquinoxalines* (I) used in the synthesis of polyphenylquinoxaline-imide-amide polymers and copolymers were prepared by the

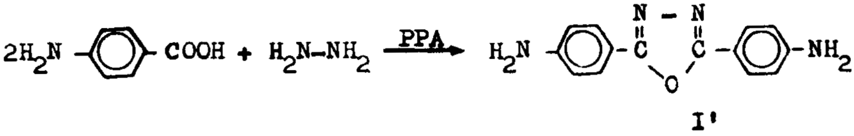


SCHEME 1.

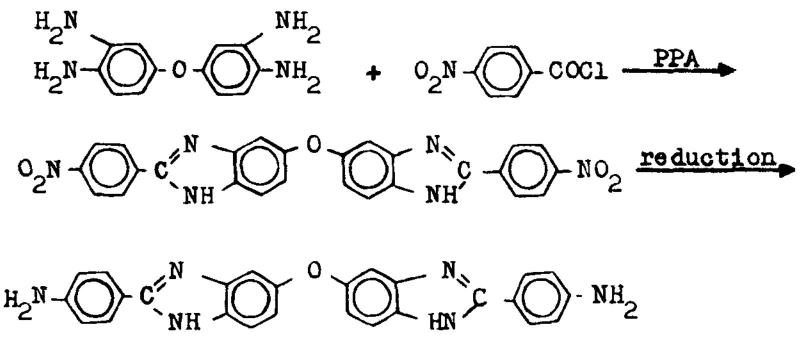
reaction of 3,4,4′-triaminodiphenylether with bis(α-diketones) [5], according to Scheme 1.

Another diamine, *2,5-bis(p-aminophenyl)-1,3,4-oxadiazole* (I′), used in the copolycondensation reaction was synthesized from *p*-aminobenzoic acid and hydrazine hydrate in polyphosphoric acid (PPA) [6] according to Scheme 2.

The third diamine used in the copolycondensation process, *2,2′-bis(p-aminophenyl)-5,5′-bis(benzimidazolyl)ether* (I″), was obtained from 3,3′,4,4′-tetraaminodiphenylether and *p*-nitrobenzoyl chloride by using polyphosphoric acid as the dehydrating reagent, following Scheme 3.



SCHEME 2.



I"

SCHEME 3.

Diacid Chlorides

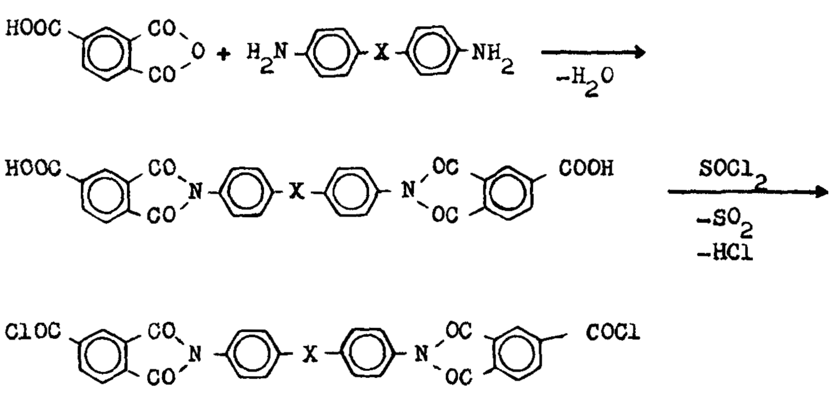
Symmetrical diacid chlorides (II) were prepared by treating with excess thionyl chloride at reflux temperature the dicarboxylic acids that resulted from the reaction of trimellitic anhydride and aromatic diamines, such as 4,4'-diaminodiphenylmethane, 4,4'-diaminodiphenylether, or 4,4'-diaminodiphenylsulfone [7], according to Scheme 4.

Nonsymmetrical diacid chlorides (II') were obtained by reacting with thionyl chloride the dicarboxylic acids which had been synthesized from *p*- or *m*-aminobenzoic acid and trimellitic anhydride [8], as shown in Scheme 5.

Synthesis of the Polymers

Polyphenylquinoxaline-Imide-Amides (PPQIA-*sym* and PPQIA-*nonsym*) were synthesized by low-temperature solution polycondensation of the equimolar amounts of diaminophenylquinoxalines (I) and diacid chlorides (II or II') in *N*-methylpyrrolidone at a concentration of 10-12%, using pyridine as an acid acceptor [9], according to Schemes 6 and 7.

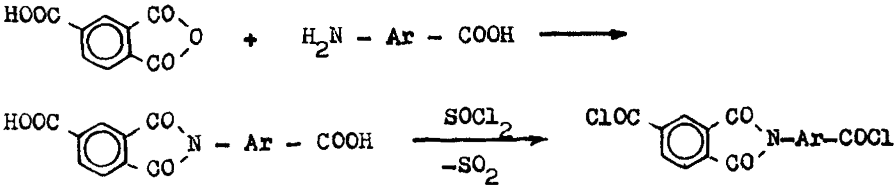
Polyphenylquinoxaline-Oxadiazole-Imide-Amides (PPQOxIA-*sym* and PPQOxIA-*nonsym*) were prepared by the same polycondensation technique of diaminophenylquinoxaline (I) and diaminooxadiazole (I') taken in the molar ratio 1:1 with diacid chloride (II or II') so that the amounts of diacid chloride and total diamine monomer were equimolar [10-12]. See Schemes 8 and 9.



II

X = $-CH_2-$, $-O-$, $-SO_2-$
(a) (b) (c)

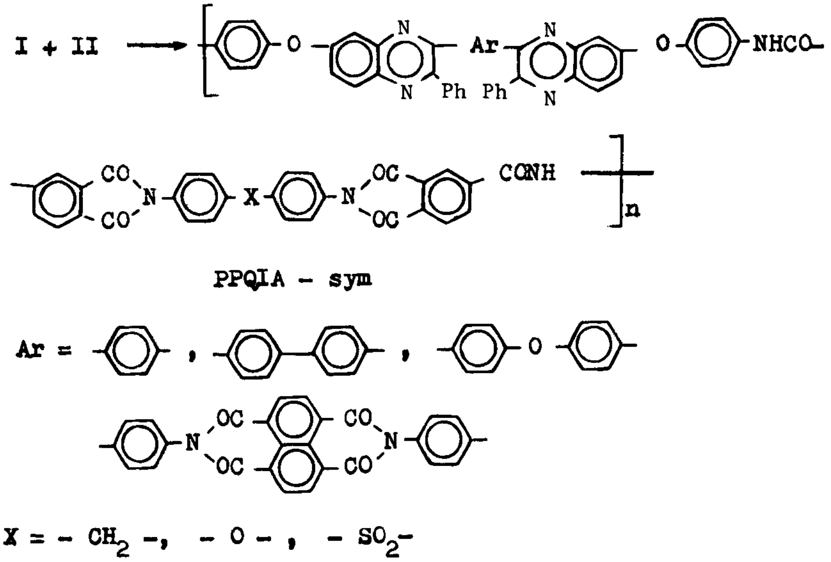
SCHEME 4.



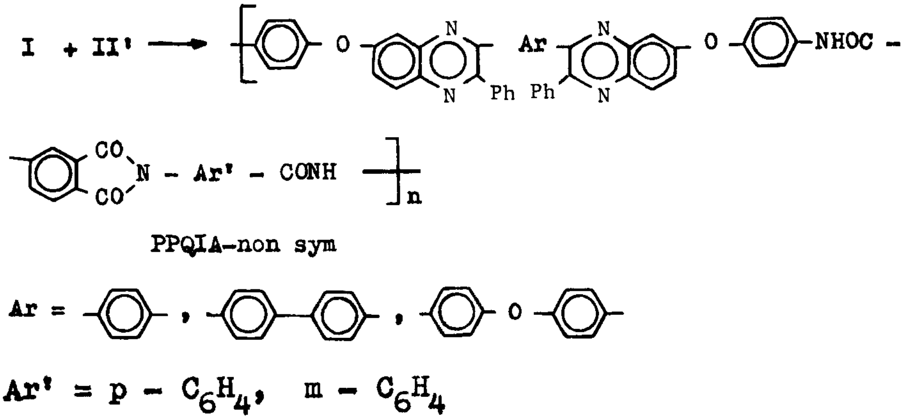
II'

Ar = p-C_6H_4, m - C_6H_4
(a) (b)

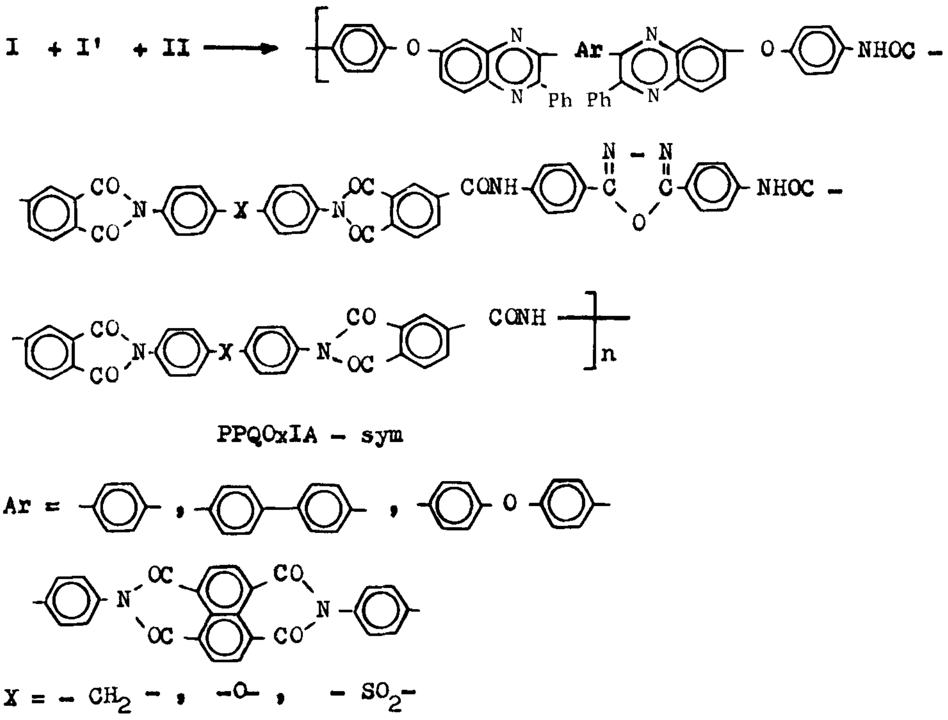
SCHEME 5.



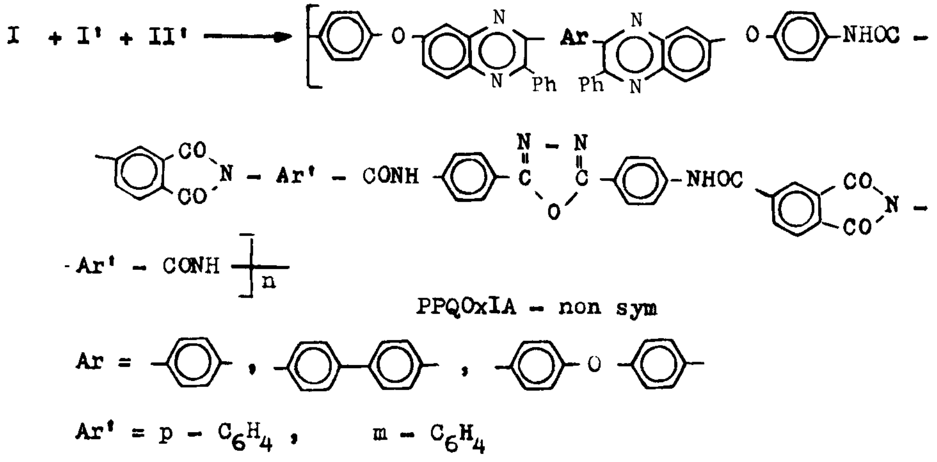
SCHEME 6.



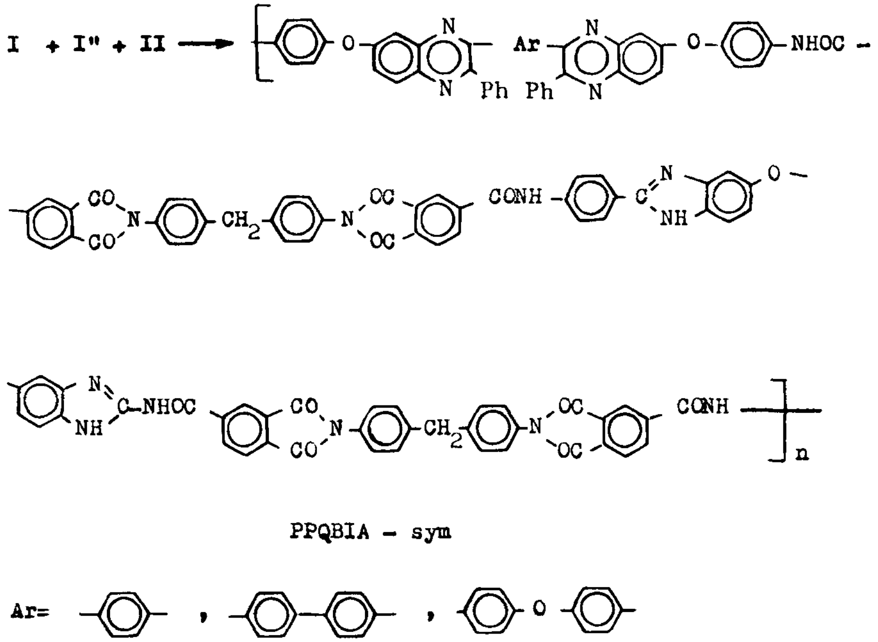
SCHEME 7.



SCHEME 8.



SCHEME 9.



PPQBIA – sym

SCHEME 10.

Polyphenylquinoxaline-Benzimidazole-Imide-Amides (PPQBIA-*sym*) were obtained by low-temperature solution polycondensation of diaminophenylquinoxaline (I_{a-c}) and diaminobenzimidazole (I'') taken in the molar ratio 1:1 with diacid chloride (II_a), so that the amounts of diacid chloride and total diamine compound were equimolar [13]. See Scheme 10.

RESULTS AND DISCUSSION

The structures of polyphenylquinoxaline-imide-amides, *co*-polyphenylquinoxaline-oxadiazole-imide-amides, and *co*-polyphenylquinoxaline-benzimidazole-imide-amides were identified by IR spectra and elemental analyses. The strong bands at 1780-1770, 1720-1710, and 720-710 cm^{-1} are assigned to the imide ring. Also, all spectra showed wide absorption bands at 3350 cm^{-1}, characteristic of NH, and at 1670-1660 cm^{-1} due to amice CO. Absorptions at 990-960 cm^{-1} in the spectra of polyphenylquinoxaline-oxadiazole-imide-amides were assigned to the oxadiazole ring, while those at 1620, 1400, and 965 cm^{-1} in the spectra of polyphenylquinoxaline-benzimidazole-imide-amides were assigned to the benzimidazole unit. Elemental analyses for C, H, N, and S are in good agreement with the calculated values.

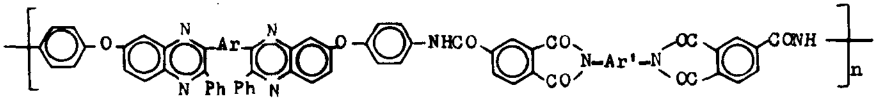
All these polymers are soluble in polar aprotic solvents, such as *N*-methylpyrrolidone (NMP) and dimethylacetamide (DMA), up to 35-40% concentration. Inherent viscosities are 0.43-1.5 dL/g, measured in *N*-methylpyrrolidone at a concentration of 0.5 g/dL at 20°C (Tables 1-6). Polymers containing SO_2 groups gave lower viscosities than those containing $-CH_2-$ or $-O-$ linkages (PPQIA-$sym_{g\text{-}i}$ in Table 1 and PPQOxIA-$sym_{g\text{-}i}$ in Table 3). This could be explained by the lower reactivity of the monomer, diacid chloride IIc, which contains SO_2 group. All these polymers gave transparent films by casting of 12-35% polymer solutions on glass plates. The films were flexible, except those prepared from polymers containing SO_2 bonds, probably due to some features of the supermolecular structure.

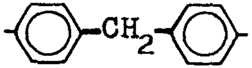
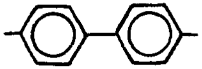
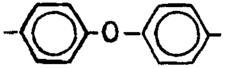
Thermogravimetric analyses of these polymers in air at a heating rate of 12°C/min show no weight loss up to 400°C (Table 6); they begin to decompose above 410°C, and at 500°C the total weight loss is 10-16%. By comparing polyphenylquinoxaline-imide-amides (PPQIA-*sym* and PPQIA-*nonsym*) with previously reported polyphenylquinoxaline-amides [5] and polyphenylquinoxaline-imides [14] with related structures, it can be seen that the thermal stability of polyphenylquinoxaline-imide-amides is somewhat lower than that of polyphenylquinoxaline-imides and similar to that of polyphenylquinoxaline-amides, which indicates that the decomposition begins with the rupture of amide linkages.

Comparison of polyphenylquinoxaline-oxadiazole-imide-amides (PPQOxIA-*sym* and PPQOxIA-*nonsym*) and polyphenylquinoxaline-benzimidazole-imide-amides (PPQBIA-*sym*) with polyphenylquinoxaline-imide-amides (PPQIA-*sym* and PPQIA-*nonsym*), which have related structures but do not contain oxadiazole nor benzimidazole units, shows that their thermal stabilities are very similar. This means that the introduction of another heterocyclic unit into the chain of polyphenylquinoxaline-amide polymers, even if this heterocycle is more thermostable, does not serve to attain higher thermostability of the final polymer.

At the same time, if we compare the present polyphenylquinoxaline-imide-amides (PPQOxIA-*sym* and PPQOxIA-*nonsym*) with polyoxadiazole-imide-amides reported earlier [8], it is noticed that the latter decompose at about 30°C higher that the former, which can be explained by strong packing between the macromolecular chains that contain only oxadiazole rings of small volume, which permits strong hydrogen bonds through amide linkages. In the related phenylquinoxaline polymers, due to the large volume of the phenyl-

TABLE 1. Properties of Polyphenylquinoxaline-Imide-Amides (PPQIA-*sym*)



				TGA		Insulating properties		
Polymer	Ar	Ar′	η_{inh}	*Initial* decomposition temperature, °C	Weight loss at 500°C, %	Dielectric loss tangent	Dielectric constant	Volume resistivity, Ω•cm
a			0.64	410	13	4.3×10^{-3}	3.12	3.45×10^{15}
b		–"–	0.82	4.35	11	4.5×10^{-3}	3.47	1.9×10^{15}
c		–"–	0.75	420	10	3.8×10^{-3}	3.2	1.07×10^{15}

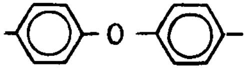
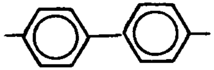
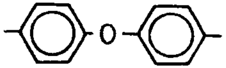
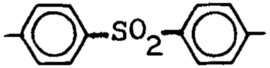
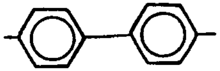
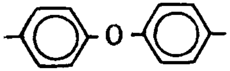
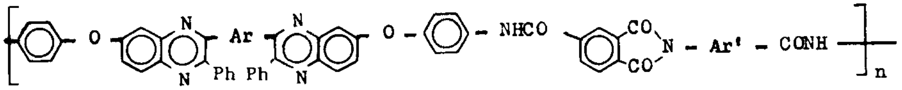
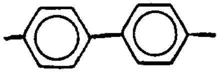
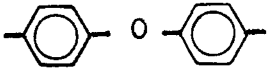
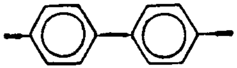
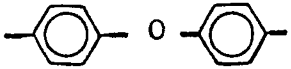
d			0.90	425	11	3.3×10^{-3}	3.6	1.01×10^{16}
e		—"—	0.96	420	11	2.9×10^{-3}	2.91	6.07×10^{16}
f		—"—	0.89	420	11	3.2×10^{-3}	2.97	8.47×10^{16}
g			0.25	410	12			
h		—"—	0.25	410	12			
i		—"—	0.26	420	12			

TABLE 2. Properties of Polyphenylquinoxaline-Imide-Amides (PPQXA-*nonsym*)



				TGA		Insulating properties		
Polymer	Ar	Ar′	η_{inh}	Initial decomposition temperature, °C	Weight loss at 500°C, %	Dielectric loss tangent	Dielectric constant	Volume resistivity, Ω•cm
a		p-C_6H_4	0.81	410	11	3×10^{-3}	2.96	3.5×10^{15}
b		”	1.1	420	10	3.1×10^{-3}	3.02	4.5×10^{15}
c		”	1.1	415	10	4×10^{-3}	3.6	1.2×10^{16}
d		m-C_6H_4	0.83	410	11	5×10^{-3}	3.24	6.6×10^{15}
e		”	0.97	415	11	4×10^{-3}	3.7	8.4×10^{16}
f		”	1.0	415	11	4.5×10^{-3}	2.98	1.5×10^{16}

quinoxaline unit, the packing of the chains is somewhat disturbed, and decomposition can begin with the scission of amide linkages, no matter what kind of other highly thermostable heterocycles are introduced into the chain. On the other band, the disturbed packing of macromolecular chains leads to better solubility. Thus, polyoxadiazole-imide-amides are difficultly soluble (only in NMP + lithium chloride), while related polyphenylquinoxaline polymers are easily soluble, at high concentration, in plain NMP.

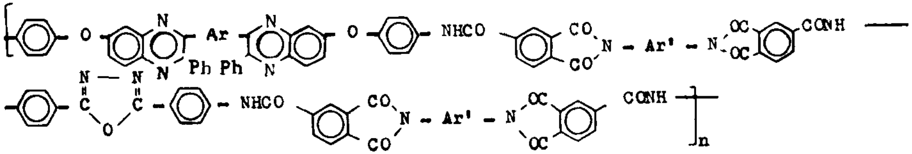
For polyphenylquinoxaline-benzimidazole-imide-amides (PPQBIA-*sym*), comparison with the other related polybenzimidazole copolymers, such as polybenzimidazole-imide-amides [15] and polybenzimidazole-imides [16], the following order was found: polybenzimidazole-imides > polyphenylquinoxaline-benzimidazole-imide-amides ≈ polybenzimidazole-imide-amides. This means that the introduction of the phenylquinoxaline unit into the chain of polybenzimidazoles gave similar thermostabilities, but the solubility of these copolymers was much improved.

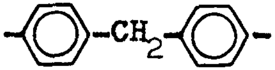
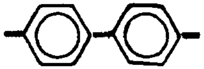
The structure of diacid chloride—symmetrical or nonsymmetrical—used in the polycondensation process influences the thermal stability of the final polymers significantly because the large volume of the phenylquinoxaline unit never allows the macromolecular chains to pack through hydrogen bonds between amide groups.

Six-membered imide rings, which are generally known for their superior thermal stability compared to five-membered imide units [17], showed no influence when introduced into the chain of polyphenylquinoxaline-amide-imides. All these facts prove that, in the present phenylquinoxaline-imide-amide polymers and copolymers, decomposition begins with the destruction of amide groups. The most important advantage of the introduction of phenylquinoxaline units into different heterocyclic polymers is their good solubility, which is very useful from a practical point of view.

Electrical insulating properties of all these polymers were studied on polymer films 30 μm thick at room temperature and a frequency of 800 Hz, using a differential bridge of type TR-9701 (Hungary) for dielectric constants and dielectric loss tangents. The dielectric loss tangents, dielectric constants, and volume resistivities evidenced good electrical insulating properties, comparable to those of polyimide film obtained from pyrromellitic dianhydride and 4,4′-diaminodiphenylether (Film H).

TABLE 3. Properties of Polyphenylquinoxaline-Oxadiazole-Imide-Amides (PPQOxIA-*sym*)



				TGA		Insulating properties		
Polymer	Ar	Ar′	η_{inh}	Initial decomposition temperature, °C	Weight loss at 500°C, %	Dielectric loss tangent	Dielectric constant	Volume resistivity, Ω·cm
a			0.9	415	12	4.8×10^{-3}	3.1	7.9×10^{15}
b		—"—	0.43	410	11	6.1×10^{-3}	2.9	4.5×10^{15}

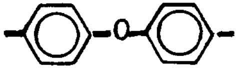
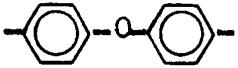
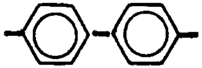
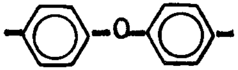
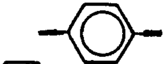
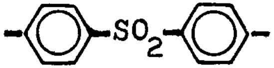
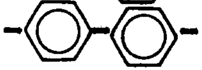
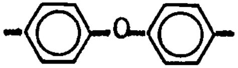
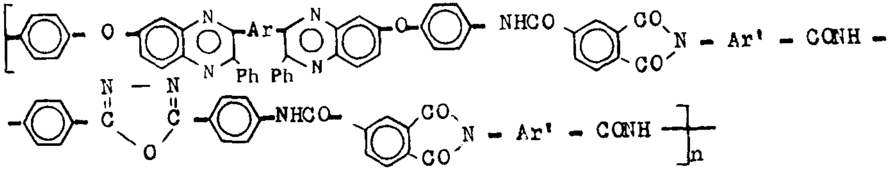
c		—"—	0.75	415	10	2.5×10^{-3}	3.2	6.3×10^{15}
d			1.5	415	12	4.1×10^{-3}	3.0	8.3×10^{15}
e		—"—	1.03	415	10	3.2×10^{-3}	2.9	3.1×10^{16}
f		—"—	1.12	420	10	2.4×10^{-3}	2.8	2.1×10^{16}
g			0.36	410	12			
h		—"—	0.35	410	12			
i		—"—	0.30	415	11			

TABLE 4. Properties of Polyphenylquinoxaline-Oxadiazole-Imide-Amides (PPQOxIA-*nonsym*)



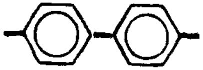
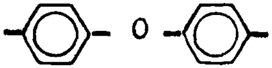
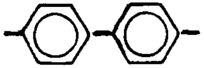
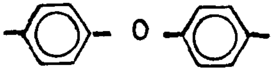
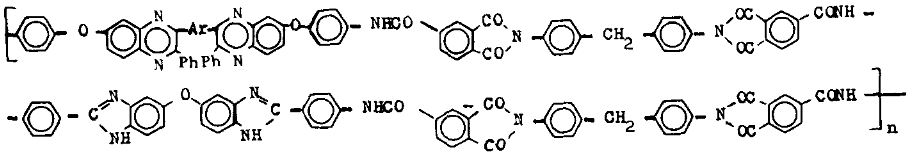
				TGA		Insulating properties		
Polymer	Ar	Ar′	η_{inh}	Initial decomposition temperature, °C	Weight loss at 500°C, %	Dielectric loss tangent	Dielectric constant	Volume resistivity, Ω·cm
a		*p*-C_6H_4	0.77	410	12	4.2×10^{-3}	3.47	3.8×10^{15}
b		”	0.85	415	11	2.9×10^{-3}	2.85	7.2×10^{15}
c		”	0.86	410	11	3.4×10^{-3}	3.1	2.8×10^{15}
d		*m*-C_6H_4	0.65	410	12			
e		”	0.69	410	12			
f		”	0.68	410	12			

TABLE 5. Properties of Polyphenylquinoxaline-Benzimidazole-Imide-Amides (PPQBIA)



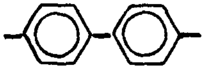
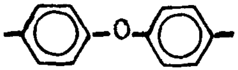
Polymer	Ar	η_{inh}	TGA Initial decomposition temperature, °C	 Weight loss at 500°C, %	Insulating properties Dielectric loss tangent	 Dielectric constant	 Volume resistivity, Ω·cm
a		0.7	415	13	6.4×10^{-3}	2.72	9.4×10^{14}
b		0.6	410	15	7.2×10^{-3}	3.6	7.0×10^{16}
c		0.6	410	16	3×10^{-3}	3.3	5.2×10^{15}

TABLE 6. Comparison of Properties of Related Polyphenylquinoxaline-Imide-Amides

		TGA		Insulating properties		
Polymer	η_{inh}	Initial decomposition temperature, °C	Weight loss at 500°C, %	Dielectric loss tangent	Dielectric constant	Volume resistivity, Ω·cm
PPQIA-*sym* (a-f)	0.64 ... 0.96	410 ... 435	10 ... 13	$2.9 \times 10^{-3} \ldots 4.5 \times 10^{-3}$	2.91 ... 3.6	$1.07 \times 10^{15} \ldots 8.47 \times 10^{16}$
PPQIA-*nonsym* (a-f)	0.81 ... 1.1	410 ... 420	10 ... 11	$3 \times 10^{-3} \ldots 5 \times 10^{-3}$	2.96 ... 3.7	$3.5 \times 10^{15} \ldots 8.4 \times 10^{16}$
PPQOxIA-*sym* (a-f)	0.43 ... 1.5	410 ... 420	10 ... 12	$2.4 \times 10^{-3} \ldots 6.1 \times 10^{-3}$	2.8 ... 3.2	$4.5 \times 10^{15} \ldots 3.1 \times 10^{16}$
PPQOxIA-*nonsym* (a-f)	0.65 ... 0.86	410 ... 415	11 ... 12	$2.9 \times 10^{-3} \ldots 4.2 \times 10^{-3}$	2.85 ... 3.47	$2.8 \times 10^{15} \ldots 7.2 \times 10^{15}$
PPQBIA-*sym* (a-c)	0.6 ... 0.7	410 ... 415	13 ... 16	$3 \times 10^{-3} \ldots 7.2 \times 10^{-3}$	2.72 ... 3.6	$9.4 \times 10^{15} \ldots 7 \times 10^{16}$
Film H				3×10^{-3}	3.5	9×10^{16}

CONCLUSIONS

Polyphenylquinoxaline-imide-amides, polyphenylquinoxaline-oxadiazole-imide-amides, and polyphenylquinoxaline-benzimidazole-imide-amides of various structures have been synthesized by low-temperature solution polycondensation of aromatic diamines containing preformed phenylquinoxaline or oxadiazole or benzimidazole units with diacid chlorides incorporating preformed imide rings. These polymers show high thermal stability, the decomposition temperature being over 400°C. Comparison of these compounds with related heterocyclic polymers leads to the conclusion that the decomposition of the former ones begins with the destruction of amide groups. The introduction of another heterocyclic unit into the chain of polyphenylquinoxaline-amides, even if this heterocycle is more thermostable, does not affect the thermal stability. Films prepared from polymer solutions showed good electrical insulating properties, comparable to those of Film H. The highest quality of these polyphenylquinoxaline-imide-amide polymers and copolymers is their remarkable solubility in polar aprotic solvents, which is very important for practical applications.

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