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AROMATIC POLYESTERAMIDES CONTAINING PHENYLQUINOXALINE UNITS

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ABSTRACT

New thermostable polymers containing phenyl substituted quinoxaline and both amide and ester groups have been synthesized by low temperature solution polycondensation of diaminophenylquinoxalines with diacid dichlorides containing preformed ester linkages.

The thermal stability as well as electrical insulating properties of these polymers are discussed and compared with related polymers previously reported.

INTRODUCTION

Among thermostable heterocyclic polymers widely studied in the last two decades, a special attention has been paid to polyquinoxalines, which showed an excellent potential for high temperature applications along with a very good storageability at ambient temperature. Moreover, phenyl substituted quinoxaline polymers have

a remarkable solubility in organic solvents which facilitates their detailed study and processing into useful materials /1, 2/.

On the other hand, heterochain polyesters and polyamides are considered to be of special practical importance due to their remarkable properties such as high heat and chemical resistance and interesting physico-mechanical properties /3, 4/. However, due to their high melting temperature and limited solubility in most organic solvents /5/, further work is necessary to develop new structures with improved processing properties, particularly with better solubility and good electrical insulating properties.

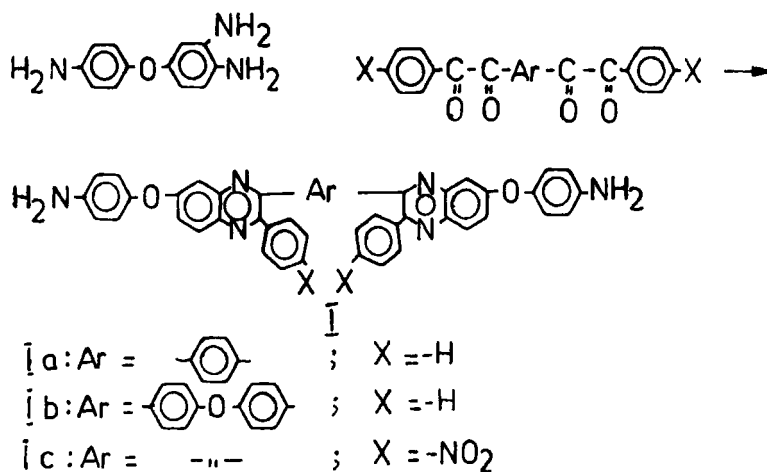
Therefore it was expected that a combination into one macromolecule of phenylquinoxaline and ester units would provide high performance physical and thermal characteristic as well as readily processable polymers. At the same time flexible groups such as amide ones introduced between aromatic and heteroaromatic rings are meant to improve even more and to generate better properties of the final materials /6/.

It is purpose of the present paper to describe the synthesis of new polymers containing phenylquinoxalines, ester and amide groups into one macromolecule and to compare their properties with related heterocyclic compounds previously reported. These polymers have been obtained by solution polycondensation of diaminophenylquinoxalines with diacid dichlorides containing preformed ester linkages using N-methylpyrrolidone as solvent.

EXPERIMENTAL

Synthesis of the monomers

Bis(aminophenylquinoxaline)s (I) used in the polycondensation reaction were prepared from 3,4,4'-triaminodiphenylether (2 mol) with bis (α -diketone)s (1 mol), such as 1,4-bis(phenylglyoxalyl)benzen, 4,4'-bis(phenylglyoxalyl)diphenylether or bis-(p-nitrophenylglyoxalyl)diphenylether in ethanol at reflux temperature, according to a method described in the literature /7/ (Scheme 1). Mp Ia: 343-345°C; Mp Ib: 157-160°C; Mp Ic: 174-175°C.



SCHEME 1

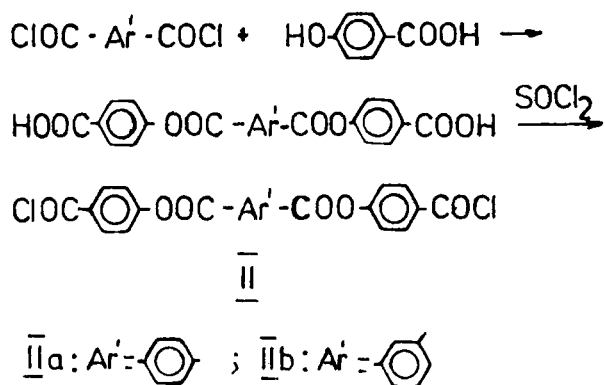
Synthesis of diaminophenylquinoxalines I

Diacid dichlorides (II) were synthesized by treating with excess thionyl chloride at reflux temperature of the corresponding dicarboxylic acids that resulted from the reaction of 4-hydroxybenzoic acid (2 mol) with terephthaloyl or isophthaloyl dichloride (1 mol), according to a method presented in the literature /8/ (Scheme 2). Mp IIa: 223-226°C; Mp IIb: 207-208°C.

Synthesis of the polymers

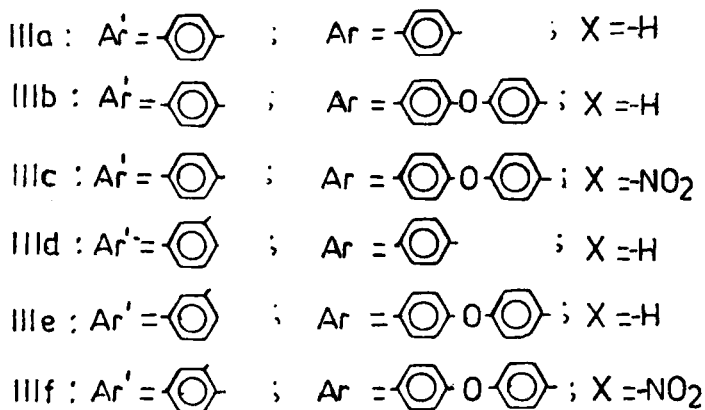
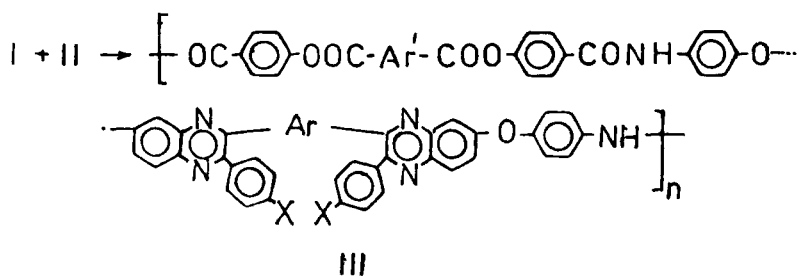
Polyphenylquinoxaline-ester-amides (II) were synthesized by solution polycondensation of equimolar amounts of bis(aminophenylquinoxaline)s (I) and diacid dichlorides (II) in N-methylpyrrolidone at a concentration of 10-12 % using pyridine as an acid acceptor, according to Scheme 3.

Polycondensations were run according to the following general procedure: A three-necked flask equipped with mechanical stirrer and N₂ inlet and outlet was charged with 2.0 mmol diamine I and 10 ml NMP. The mixture was stirred under nitrogen until complete



SCHEME 2

Synthesis of diacid dichlorides II



SCHEME 3

Synthesis of aromatic polyamides containing phenylquinoxaline units III

dissolution occurred. Then the solution was cooled to -5°C , and 2.0 mmol diacid dichloride II was added with rapid stirring. The reaction temperature was maintained below -5°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 x 200 mm), and after evaporating the solvent and drying in an oven at 100°C for 30 minutes, 150°C for 1 hour 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.

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, using an Ubbelohde viscometer.

Infrared Spectra of the polymers were recorded on a SPECORD M-80 Spectrophotometer using KBr pellets.

Glass transition temperatures (T_g) of precipitated polymers were determined with a Seiko differential scanning calorimeter DSC 220C.

Thermal stability was investigated using a MOM derivatograph (Hungary) in air at a heating rate of $12^{\circ}\text{C}/\text{min}$.

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

RESULTS AND DISCUSSION

The structures of poly(phenylquinoxaline-ester-amide)s (III) were identified by IR spectra and elemental analysis. Strong bands appeared at 1750 cm^{-1} , 1610 cm^{-1} , 1200 cm^{-1} and 1170 cm^{-1} are assigned to the COO linkage. All the IR spectra showed wide absorption bands from 3500 to 3300 cm^{-1} with a maximum at around 3470 cm^{-1} characteristic for NH and at 1670 cm^{-1} due to C=O in the amide group. The polymers IIIc and IIIf have presented strong bands at 1510 and 1350 cm^{-1} due to NO_2 group. The IR spectrum of polymer IIIf illustrates these features (Figure 1).

Elemental analysis data for C, H, N are in good agreement with the calculated values (Table 1).

Poly(phenylquinoxaline-ester-amide)s are soluble in polar aprotic solvents such as NMP, DMAc, DMF up to 30-40 % concentration. The improved solubility of these polymers can be explain 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 small solvent molecules can penetrate easily to solubilize the chains /10/.

Inherent viscosity are $0.52 - 0.825\text{ dL/g}$ in NMP at a concentration of $0.5\text{ g polymer}/100\text{ ml}$ solution at 20°C (Table 1). All these polymers gave transparent flexible films by casting 10 % polymer solutions onto glass plates.

The thermal stability of poly(phenylquinoxaline-ester-amide)s was evaluated by thermogravimetric analysis performed in air at a heating rate of $12^\circ\text{C}/\text{min}$. Polymers showed no significant weight loss up to 370°C ; they begin to descompose above 380°C . At 400°C and 500°C the total weight loss was 4-6 % and 18-25.5 % respectively (Table 2).

By comparing these compounds containing only aromatic units in the main chain with poly(phenylquinoxaline-ester-imide)s /11/ incorporating both aromatic and aliphatic units it can be seen that the thermal stability of the former is about 25°C higher than the later.

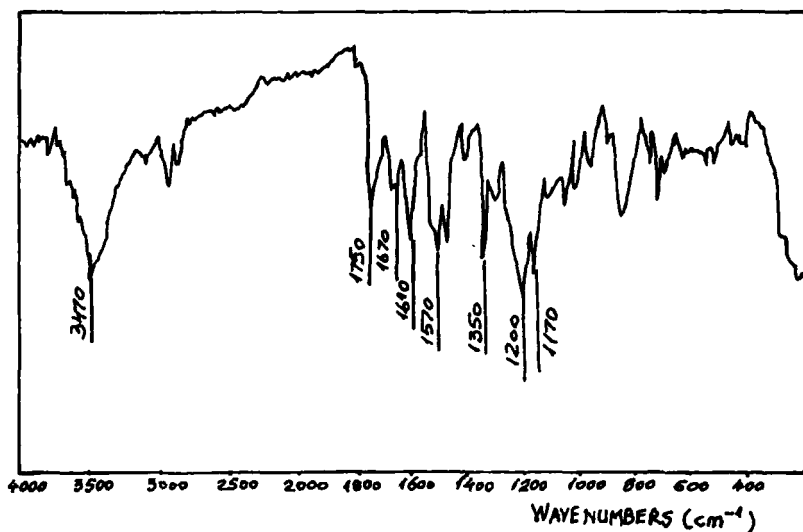


FIGURE 1

IR spectrum of polyphenylquinoxaline-ester-amide IIIf

Table 1
Inherent viscosity and elemental analysis of the
aromatic polyesteramides

Polymer	η_{inh} (dL/g)	Elemental analysis					
		C %		H %		N %	
		Calcd.	Found	Calcd.	Found	Calcd.	Found
IIIa	0.825	76.26	75.39	3.92	4.08	7.85	7.56
IIIb	0.629	76.41	75.42	3.95	3.80	7.22	7.20
IIIc	0.600	70.92	70.93	3.51	3.70	8.94	8.50
III d	0.580	76.26	74.52	3.92	4.15	7.85	7.70
IIIe	0.565	76.41	75.18	3.95	4.29	7.22	7.18
III f	0.525	70.92	70.79	3.51	3.75	8.94	8.72

Table 2
Thermal properties of the aromatic polyesteramides
containing phenylquinoxaline units

Polymer	Initial decomposition temperature (°C)	Weight loss at		T _g (°C)
		400°C (%)	500°C (%)	
IIIa	395	4	18.0	250
IIIb	390	5	17.5	238
IIIc	385	9	21.0	258
IIId	390	5	26.5	250
IIIe	385	4	22.5	230
IIIf	375	6	24.0	-

This is explained by the well known vulnerability of aliphatic chains towards thermooxidative processes.

At the same time comparison of the present polymers with related aromatic polyesterimides /12/ and with poly(phenylquinoxaline-ester-imide)s incorporating only aromatic units in the backbone /6, 13/ shows that their thermal stabilities are very similar. Indeed, aromatic polyesterimides are little soluble, only in NMP + LiCl while the poly(phenylquinoxaline-ester-amide)s are easily soluble in plain NMP at high concentration which is very important for practical applications.

Glass transition temperatures (T_g) of the present poly(phenylquinoxaline-ester-amide)s, are in the range of 230-260°C. These values are with about 40°C lower than the T_g of polyphenylquinoxaline-imide-amides /10/, and it can be explain by the large number of flexible groups, ester and amide, which are incorporated in the chain of present polymers. The large temperature range between T_g and the decomposition temperature makes the polymers attractive for processing.

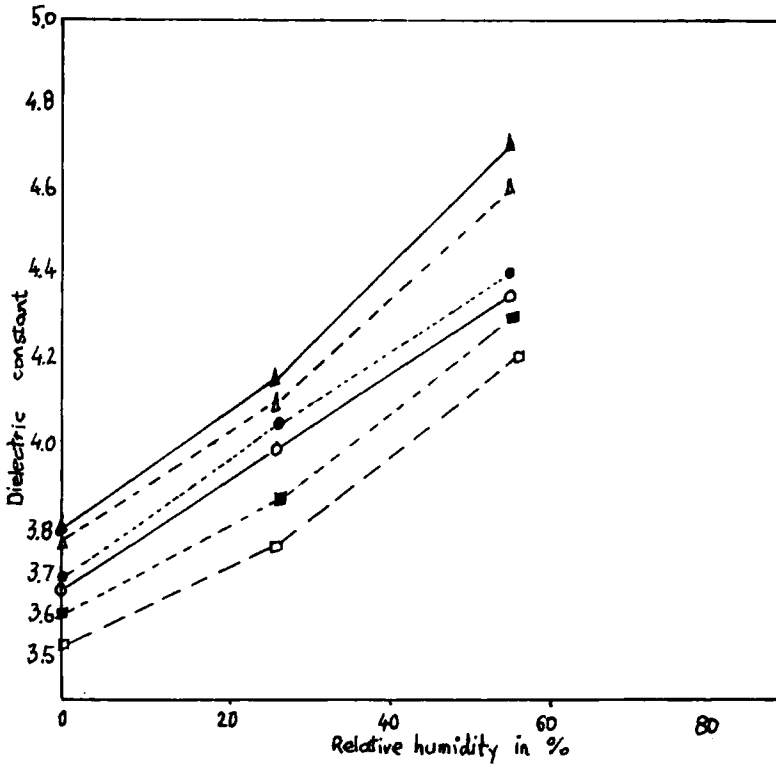


FIGURE 2
Dielectric constant vs. relative humidity for films of poly(phenylquinoxaline-ester-amide)s (o) IIIa; (□) IIIb; (Δ) IIIc; (●) IIId; (■) IIIe; (▲) IIIf.

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 3.5-3.8 range. These values are slightly higher than the dielectric constant of the polyimide film (H) prepared from pyromellitic dianhydride and 4,4'-diaminodiphenyl-ether /14/ and from Ultem type polyimides, e.g., Ultem 1000 dielectric constant is 3.15 /15/. The dependence of the dielectric constants versus relative humidity is shown in Figure 2.

From the plotted values, one can observe that polymers IIIc and IIIf, which contain pendent nitro groups have the highest dielectric constants. There are number of factors affecting the dielectric properties of materials. The dielectric constant of a polymer is a function of the total polarizability /16/; these polymers displaying higher dielectric constants have higher polarizability.

CONCLUSIONS

New thermostable polymers constaining phenylquinoxaline, ester and amide groups have been synthesized by solution polycondensation of diaminophenylquinoxaline with diacid dichlorides containing preformed ester linkages. These polymers are soluble in polar aprotic solvents and give transparent flexible films with good electrical insulating properties. They decompose over 380°C and have a glass transition temperature in the 230-260°C range.

REFERENCES

1. E.S.Krongauz, Vysokomol. Soedin. A 26, 227 (1984).
2. P.Hergenrother, Encycl. Polym.Sci.Eng., Vol.13, 55 (1988).
3. J.Economy, J.Macromol.Sci.Chem. A 21, 1705 (1984).
4. J.Preston, Encycl. Polym.Sci.Eng., Vol. 11, 381 (1988).
5. W.J. Jackson, Br.Polym.J., 12, 154 (1980).
6. M.Bruma, I.Sava, C.Hamciuc, C.I.Simionescu, N.M.Belomoina, S.A.Babich, E.S.Krongauz, Acta Polym., 42, 125 (1991).
7. V.V. Korshak, E.S.Krongauz, N.M.Belomoina, H.Raubach, D.Hein, Acta Polym., 34, 213 (1983).
8. A.Bilibin, A.Tenkovtsev, O.Piraner, Vysokomol. Soedin., A 26, 2570 (1984).
9. F.W. Mercer and T.D.Goodman, High Performance Polym., 3, 297 (1991).
10. M.Bruma, I.Sava, W.H.Daly, F.W.Mercer, I.I.Negulescu, J.Macromol. Sci.-Pure Appl.Chem., A 30, 789 (1993).

11. M.Bruma, I.Sava, C.Hamciuc, C.I.Simionescu, N.M.Belmoina, E.S.Krongauz, V.V.Korshak, Rev.Roum.Chim., 34, 1467 (1989).
12. M.Bruma, I.Sava, Rev.Roum.Chim., 30, 239 (1985).
13. I.Sava, E.Hamciuc, C.Hamciuc, M.Bruma, C.I.Simionescu, N.M. Belmoina S.A.Babich, Rev.Roum.Chim., 37, 1145 (1992).
14. C.E.Sroog, J.Polym.Sci.-Macromol.Rev., 11, 161 (1976).
15. J.W.Verbiki Jr., "Polyimides", in Concise Encyclopedia of Polymer Science and Engineering (J.I.Kroschwitz, Exec.Ed.), Wiley, New York, p. 826 (1990).
16. G.Hougham, G.Tesoro, A.Viehbeck and J.Chapple-Sokol, Polymer Preprints, 34, 375 (1993).