

SYNTHESIS AND PROPERTIES OF POLYPHENYL-QUINOXALINES CONTAINING CHLORO-ATOM

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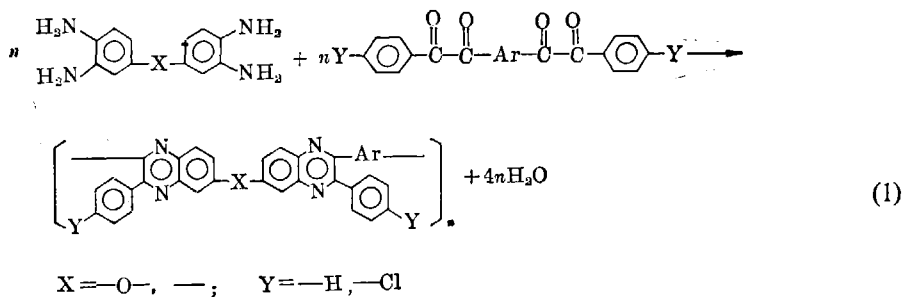
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ABSTRACT

Several polyphenylquinoxalines (PPQ's) containing chloro-atom in the side chain have been synthesized and characterized by IR, TGA, ITGA and DTA. High quality, flexible, glass-cast films and varnished wires have been obtained. The T_g 's values and thermal stabilities of these polymers were greater than those without any chloro-atom substituent.

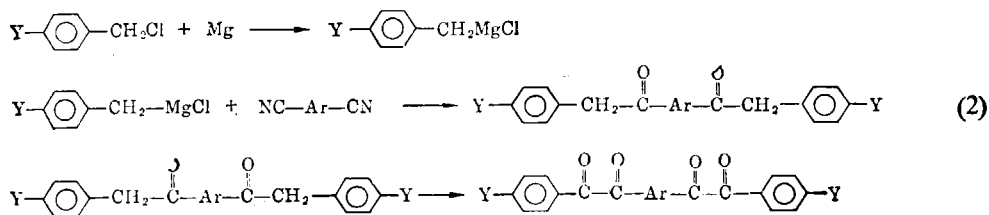
Polyphenylquinoxaline and polyimide both are well known heat resistant polymer, but the former possesses excellent hydrolytic stability while the latter is completely hydrolyzed under the same experimental condition^[1]. However, the linear PPQ's remain thermoplastic at high temperature although they have high thermal and oxidative stabilities. Work has been performed to overcome this shortcoming by thermal crosslinking with cyano or acetylene terminated group in literature^[2]. The objective of this effort was to evaluate the effectiveness of chloro-atom in the polymer structure to postpone high temperature thermoplasticity. Experimentally, several new PPQ's containing chloro-atom in the side chain have been synthesized and characterized by infra-red spectroscopy, differential thermal analysis, and thermogravimetric analysis. The T_g 's and thermal stability of such PPQ's are higher than those without any chloro-atom substituent. Thus both the PPQ's previously prepared^[3] and the PPQ's containing chloro-atom possessed good thermal stability, hydrolytic stability, chemical and oil resistant properties.

A series of polyphenylquinoxalines (PPQ's) containing chloro-atom was synthesized from the solution cyclopolycondensation of aromatic tetraamines with various 4,4'-dichloro dibenzils according to Eq. (1):



The 4,4'-dichloro dibenzils were synthesized by using 4,4'-dicyano aromatic compounds as the starting materials which reacted with Grignard reagent of 4-chlorobenzil chloride and were then oxidized by dimethyl sulfoxide (DMSO) in the presence of hydrobromic acid. It was a simplified procedure, and gave high purity^[3,5] as compared with the commonly used oxidizing agent such as SeO_2 in the literature.

The route used to prepare 4,4'-dichloro dibenzils are shown in Eq. (2):



Aromatic tetraamines were prepared by known method^[9].

EXPERIMENTAL

Monomers

4,4'-Bis(4"-chlorophenylglyoxalyl)diphenylene was synthesized according to our previous work^[3,4], m.p. 286–288°C. Anal. Calcd for $(\text{C}_{28}\text{H}_{16}\text{O}_4\text{Cl}_2)$: C, 69.01%; H, 3.31%; Cl, 14.55%. Found: C, 69.28%; H, 3.45%; Cl, 14.30%.

4,4'-Bis(4"-chlorophenylglyoxalyl)diphenyl ether was prepared following a known procedure^[5], m.p. 171.5–173.0°C. Anal. Calcd for $(\text{C}_{28}\text{H}_{16}\text{O}_5\text{Cl}_2)$: C, 66.81%; H, 3.20%; Cl, 14.08%. Found: C, 66.55%; H, 3.11%; Cl, 13.94%.

1,4-Bis(4'-chlorophenylglyoxalyl)benzene was prepared by the method in literature^[6,7], m.p. 279–280°C. Anal. Calcd for $(\text{C}_{22}\text{H}_{12}\text{O}_4\text{Cl}_2)$: C, 64.25%; H, 2.94%; Cl, 17.24%. Found: C, 64.04%; H, 2.88%; Cl, 17.21%.

3,3'-Diaminobenzidine (DAB) was obtained by purification of the commercial product, m.p. 175–176°C (Lit.^[8] 179–180°C).

3,3',4,4'-Tetraaminodiphenyl ether was prepared in our laboratory, m.p. 151–152°C (Lit.^[9] 149.5–151.0°C).

Polymers

Poly[2,2'-(p,p'-diphenyl ether)-6,6'-oxybis(3-chlorophenylquinoxaline)] (I). It was prepared by polymerization of 0.5870g (2.549 mmol) of 3,3',4,4'-tetraaminodiphenyl ether (TADPE), 1.2832g (2.549 mmol) of 4,4'-bis(4"-chlorophenylglyoxalyl)diphenyl ether and 13g of cresol under N_2 by vigorous stirring at room temperature for 2 hours, a transparent brown polymer solution was obtained.

Poly[2,2'-(p,p'-diphenylene)-6,6'-oxybis(3-chlorophenylquinoxaline)] (II). 0.3520g (1.529 mmol) of TADPE was reacted with 0.7452g (1.529 mmol) of 4,4'-bis(4"-chlorophenyl-

glyoxalyl) diphenylene in 8g of cresol under N_2 by vigorous stirring at $120^\circ C$ for 3 hours, transparent brown polymer solution was formed.

Poly[2,2'-(p,p'-phenyl)-6,6'-oxybis(3-chlorophenylquinoxaline)] (III). The transparent brown polymer solution was prepared by the polymerization of 0.6102g (2.65 mmol) of TADPE with 1.0899g (2.65 mmol) of 1,4-bis(4'-chlorophenylglyoxalyl) benzene in 13g of cresol under N_2 with vigorous stirring at $160^\circ C$ for 3 hours.

Poly[2,2'-(p,p'-diphenyl ether)-6,6'-bis(3-chlorophenylquinoxaline)] (IV). The procedure used to prepare polymer (IV) was the same as that of polymer (I).

Poly[2,2'-(p,p'-phenyl)-6,6'-bis(3-chlorophenylquinoxaline)] (V). The preparation of polymer (V) was the same as that of polymer (III).

Film was prepared from the polymer solutions by casting a portion of the cresol solution onto a glass plate, followed by evaporating the solvent in air at $80-90^\circ C$ and then cured at $300^\circ C$ for 2 hours under N_2 . The varnished wire was obtained by coating the polymer solution on metallic wire and curing by a rolling machine in air. Both of the these films and coated wires were used for determining properties of polymers.

RESULTS AND DISCUSSION

Since the solubilities of monomers in cresol are quite different, so the polymerization of two monomers was carried out at ambient temperature (polymer I, IV) for 2 hours, at $120^\circ C$ (polymer II) or at $160^\circ C$ (polymer III, V) for 3 hours under N_2 respectively. The reaction mixture is generally left standing overnight at ambient temperature to provide a viscous stable solution of high molecular weight. η_{inh} was determined. The resulting solution can be

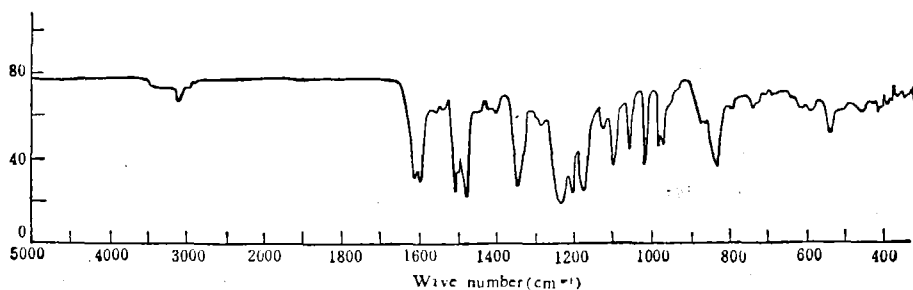


Fig. 1 IR spectrum of polymer (I)

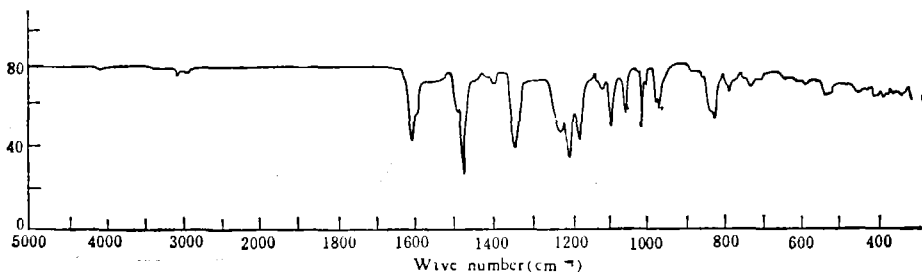
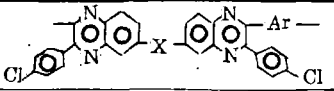
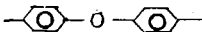
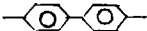
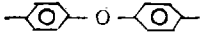


Fig. 2 IR spectrum of polymer (II)

used directly in application work for film casting and wire coating. The IR spectra of amino and carbonyl groups disappeared as shown in Figs. 1 and 2.

The glass transition temperature (T_g), polymer decomposition temperature (PDT) and tensile strength are shown in Table 1.

Table 1 Properties of PPQ's containing chloro-atom

No.			$\eta_{inh}^{1)}$ (dl/g)	$T_g^{2)}$ (°C)	PDT ³⁾ (°C)	Tensile tear strength (kg/cm ²)
	X	Ar				
I	—O—		1.70	234	531	1137
II	—O—		1.52	336	533	1202
III	—O—		0.58	325	530	1023
IV	—		0.64	320	544	1116
V	—		0.82	362	554	1433

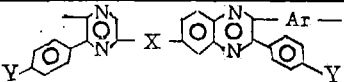
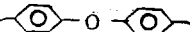
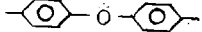
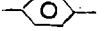
1) Inherent viscosity (0.5% in cresol at 30°C).

2) T_g was determined by DTA, the rate of heating: 10°C/min.

3) Polymer decomposition temperature (PDT) was determined by TGA, the rate of heating: 10°C/min.

Obviously, the T_g 's of PPQ's containing chloro-atom in the side chain are higher than those without chloro-atom substituents. For example, the T_g of polymer (III) is equal to 325°C while that of polymer (VI) is 310°C^[3]. The PDT's of these polymers determined by thermogravimetric analysis (TGA) were about 530–554°C. The polymers were isothermally heated at 300°C in air over different time periods. ITGA results, shown in Table 2, indicated that the weight loss of polymer (III) or polymer (V) is less than that of polymer (VI) or polymer (VII). This means that the thermal oxidative stability of PPQ containing chloro-atom is better than that of the general linear PPQ with corresponding chemical main chain structure.

Table 2 Isothermal aging of PPQ's containing chloro-atom in air

No.				Wt. loss at 300°C (%)			
	X	Ar	Y	50	100	150	200h
I	—O—		Cl	0.43	0.52	0.84	0.88
II	—O—		Cl	0.46	0.53	0.74	0.83
III	—O—		Cl	0.53	0.63	1.02	1.12
IV	—		Cl	0.41	0.48	0.63	0.72
V	—		Cl	0.55	0.74	0.85	0.96
VI	—O—		H	0.54	0.82	1.24	1.43
VII	—		H	0.58	0.65	1.12	1.27

Due to the good flexibility of these polymers, the varnished wires were made by coating the polymer solution on the metallic wires. The thickness of the coating was about 20—35 μ . The coating retained good electric insulation after being boiled in water for 4000 hours, in 40% sodium hydroxide solution and heated in polymethylsiloxane for 24 hours respectively, as shown in Table 3.

Table 3 Insulation resistance (Ω) of PPQ's containing chloro-atom

No.	Methyl silicon oil ¹⁾		40% KOH ²⁾		5% HCl		Boiling water 4000 h
	0 h	24 h	0 h	24 h	0 h	24 h	
I	3.8×10^{12}	8.0×10^{12}	2.4×10^{11}	9.0×10^{11}	9.0×10^{12}	$>10^{12}$	—
II	2.0×10^{12}	1.0×10^{12}	2.8×10^{11}	5.0×10^{10}	9.0×10^{12}	$>10^{12}$	5.0×10^{12}
V	3.0×10^{12}	2.8×10^{12}	8.0×10^{10}	6.0×10^{10}	9.0×10^{12}	$>10^{12}$	—

1) At 80°C; 2) At reflux temperature.

REFERENCES

- [1] Lu Fengcai, Liang Desheng, Lai Zhugen, Bai Luna and Gao Yuanming, *Scientia Sinica (Series B)*, **1986**, Vol. XXIX, No. 4, 345.
- [2] De la Camps, J. G., De Abajo, *J. Rev. Plast. Mod.*, **1983**, 46 (328), 396, 407 (Span).
- [3] 卢凤才、哇秀楣、王百庚、张金彪、邢兰敏、王玉兰、高元明、白路娜, 高分子通讯 (*Polymer Communications*), **1980**, (3), 146.
- [4] Xing Lanmin, Bai Luna and Lu Fengcai, *Polymer Communications*, **1985**, (2), 50.
- [5] 邢兰敏, 卢凤才, 有机化学, **1983**, (6), 447.
- [6] 孙猛、陈文基、金瑚珍、杨玉良, 高分子通讯 (*Polymer Communications*), **1982**, (6), 447.
- [7] AD-A039083, **1976**.
- [8] Vogel, H. and Marvel, C. S., *J. Polym. Sci.*, **1961**, 50, 529.
- [9] Foster, R. and Marvel, C. S., *J. Polym. Sci.*, **1965**, A3, 419.
- [10] Hergenrother, P. M., *Polymer Preprints*, **1974**, 15 (1), 781.