

INCORPORATION OF METAL IONS INTO POLYPHENYLQUINOXALINE*

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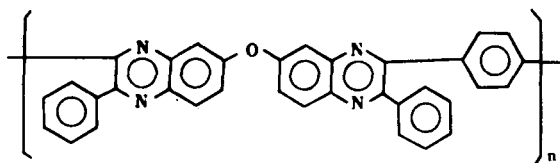
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ABSTRACT

$\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, NiCl_2 , CuCl_2 , ZnCl_2 and CrCl_3 have been incorporated into polyphenylquinoxaline by a new method. High-quality, flexible, glass-cast films have been obtained which exhibit increased glass transition temperature and excellent thermal stability. Moduli and tensile strengths of the metal-containing polyphenylquinoxaline films increase surprisingly at elevated temperature. Electrical resistivities of these films fall in the same order range as polyphenylquinoxaline alone. X-ray photoelectron spectroscopic study of metal-containing polyphenylquinoxaline films shows that all metals in these films are present in the ionic state, there is charge transfer between nitrogen of polyphenylquinoxaline and Cu^{2+} , Zn^{2+} of CuCl_2 , ZnCl_2 containing polyphenylquinoxaline films.

The continuing demand for materials with a unique combination of properties has brought forth much research effort^[1] concerning polymer modification via incorporation of a variety of non-metallic and metallic dopants into the polymer. Metallic additives included metal-atom vapor, metal salts, metal complexes and organometallic compounds. Polymer systems studied to date include polyamides, polyimides, poly(alkylbenzimidazoles), poly(vinyl alcohol), polyethers, polyesters, polyacetylene, poly(p-phenylene), polyethylene and polysiloxane^[2]. From the very limited number of studied available, it is quite apparent that metallic additives may have a profound effect on polymer properties. Different metals as well as different additives of the same metal can induce a variety of physical and chemical changes in a given polymer. Subtle difference in the polymer backbone can even significantly alter the metal dopant effect for a certain class of polymer. Hence the modification of polymer properties via metal incorporation certainly requires further study.

Polyphenylquinoxaline has excellent thermal stability and chemical resistance, water resistance along with electric insulation^[3]. Metal chlorides containing polyphenylquinoxaline(PPQ) have been recently prepared using a new method for the purpose of modifying their high temperature properties in our laboratory. Metal chlorides containing polyphenylquinoxaline have been partially characterized. The results of this study are described as follows.



PPQ

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EXPERIMENTAL

Materials

$\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, ZnCl_2 , $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ were obtained from commercial sources and dried at 100°C in vacuum for four hours to obtain NiCl_2 , CuCl_2 , ZnCl_2 and CrCl_3 . $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ was also obtained from commercial sources. Polyphenylquinoxaline was prepared from tetraamine and tetraketone according to literature[3].

Incorporating metal chloride into PPQ

Incorporation of metal chloride into PPQ was carried out by adding PPQ (0.001 mol) and metal chloride (0.001 mol) into a mixed solvent containing 25 ml 1, 1, 2, 2-tetrachloroethane (TCE) and 5 ml anhydrous ethanol. The solution was stirred at 80°C for four hours. The resulting solution was transparent.

Preparation of Films

(A) Preparation of PPQ- NiCl_2 , PPQ- ZnCl_2 or PPQ- CrCl_3 films.

PPQ-metal chloride solutions were evaporated in vacuum to remove ethanol, the residual solutions were also transparent and poured onto glass plates. Films of the PPQ-metal chloride thus formed were redissolved in TCE-chloroform (volume ratio = 1:1). The solutions were filtered to remove the excess metal chlorides. The filtrates were then poured onto glass plate to form films of PPQ-metal chloride by drying in air at 60°C overnight. Curing was thermally achieved by heating under Ar for 1 hour at 300°C . PPQ-metal chloride films were removed from the glass plates after soaking in cold water for several hours. By using the same method to prepare PPQ- FeCl_3 and PPQ- CuCl_2 films gel or powder resulted instead of film.

(B) Preparation of PPQ- FeCl_3 and PPQ- CuCl_2 films.

PPQ-metal chloride solutions were precipitated by adding a large amount of ethanol and filtered. The powders were rinsed by fresh ethanol three times, dried in air at 80°C and then dissolved in TCE-chloroform (volume ratio = 1:1). PPQ- FeCl_3 and PPQ- CuCl_2 films were prepared in the same way as described in method (A).

Characterization

Thermogravimetric analyses of the films were made at the temperature increasing rate of $10^\circ\text{C}/\text{min}$ in static air. Tensile tests of the films at room temperature and at 200°C were performed on an Instron 1122 and Instron 1195. For high temperature tests each film specimen was soaked for 15 minutes at 200°C before testing. X-ray photoelectron spectra (XPS) were obtained on an ESCA-650B spectrometer equipped with a Mg anode ($\text{Mg } K_\alpha = 1253.6 \text{ eV}$) target. The binding energies of all electrons were measured relative to the instrumental background carbon (C_{1s}) photopeak taken to be 285.0 eV.

RESULTS AND DISCUSSION

The usual method of incorporating metallic compounds into neutral polymer requires a solvent in which the polymer and the metallic compounds to be incorporated are both soluble. Just as many other aromatic heterocyclic polymers PPQ can be dissolved only in m-cresol, TCE, chloroform or concentrated sulfuric acid. However most metallic compounds are not soluble in these solvents. So the usual method is not suitable for PPQ. This paper presents a new method to

incorporate metal salts into PPQ by using a solvent which is a mixture of TCE and ethanol in volume ratio of 5 to 1. The PPQ is soluble in the former solvent while the metal salts are soluble in the latter. Twelve metal (Fe, Co, Ni, Cu, Zn, Mn, Cr, La, Ce, Sn, Rh, Pt) chlorides or sulfates insoluble in TCE have been incorporated into PPQ in this mixed solvent and could form high quality flexible films. In this regard, we wish to describe the $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, NiCl_2 , CuCl_2 , ZnCl_2 and CrCl_3 containing PPQ films. These PPQ films were flexible and their colours varied with different metal ions (Table 1). There was no apparent change in chemical properties as judged by infrared spectra comparisons of the doped and undoped polymer.

Table 1 Physical properties of PPQ-metal chloride films

PPQ-metal chloride Film	Thickness(μ)	Result
PPQ alone ¹⁾	46.2	Flexible, light yellow
PPQ- FeCl_3	46.7	Flexible, dark brown red
PPQ- NiCl_2	50.9	Flexible, brown
PPQ- CuCl_2	51.0	Flexible, red brown
PPQ- ZnCl_2	54.0	Flexible, dark brown
PPQ- CrCl_3	35.0	Flexible, dark brown

1) η_{inh} 2.56 dl/g (0.5% in cresol at 30°C)

The effects of the five different metal chlorides on glass transition temperature (T_g) and polymer decomposition temperature (PDT) are shown in Table 2. The T_g of the doped polymer films was 14–50°C higher than that of the undoped polymer with the exception of CrCl_3 -containing films.

Inspection of the data (Table 2) reveals that the T_g 's of PPQ- FeCl_3 , PPQ- NiCl_2 , PPQ- CuCl_2 and PPQ- ZnCl_2 increase without sacrificing thermal stability. Significant thermal stability has been sacrificed in PPQ- CrCl_3 and there was no T_g to be detected.

Table 2 Thermal properties of PPQ-metal chloride films

PPQ-metal chloride Film	$T_g(^{\circ}\text{C})^{1)}$	PDT($^{\circ}\text{C})^{2)}$	%Metal ³⁾
PPQ alone	310	531	
PPQ- FeCl_3	360	512	0.99
PPQ- NiCl_2	324	513	6.0
PPQ- CuCl_2	320	522	0.29
PPQ- ZnCl_2	325	516	1.3
PPQ- CrCl_3	—	427	3.4

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

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

3) Metal contents were measured by atomic absorption spectrometry.

Table 3 Isothermal studies of PPQ-metal chloride films*

PPQ-metal chloride film	% Weight loss
PPQ alone	3.82
PPQ-FeCl ₃	24.12
PPQ-NiCl ₂	4.18
PPQ-CuCl ₂	91.18
PPQ-ZnCl ₂	3.34
PPQ-CrCl ₃	55.26

* Isothermal aging of PPQ's films at 320°C in air for 50 hours.

These observations of thermal stability are further studied by isothermal measurements on these films at 320°C for 50 hours in air. The PPQ-FeCl₃, PPQ-CuCl₂, PPQ-CrCl₃ films did not survive isothermal aging of the environment. Even though PPQ-FeCl₃, PPQ-NiCl₂, PPQ-CuCl₂ and PPQ-ZnCl₂ films exhibit about the same polymer decomposition temperature by dynamic TGA, the PPQ-NiCl₂ and PPQ-ZnCl₂ films are noticeably more thermally stable by isothermal measurement. Inspection of Tables 2,3 reveals that the glass transition temperature of these two doped polymers increases without any loss in thermal stability.

Mechanical properties of these metal-containing PPQ films have been measured. The tensile strengths for these films are given in Table 4. The tensile strengths of all metal-containing films are high. At elevated temperature metal-containing films have surprisingly increased strengths. Tensile modulus and percent elongation for these films are given in Table 5. The latter generally decrease in comparison with the undoped polymer both at room temperature and 200°C. The tensile moduli of all these metal doped polymer films increase irrespective of the test temperature and the nature of dopants.

Table 4 Mechanical properties of PPQ-metal chloride films

PPQ-metal chloride film	Tensile strength (kg/cm ²)	
	RT	200°C
PPQ alone	1213	470
PPQ-FeCl ₃	1185	480
PPQ-NiCl ₂	1254	525
PPQ-CuCl ₂	1286	524
PPQ-ZnCl ₂	1352	564
PPQ-CrCl ₃	1287	—

On the other hand, the volume resistivity of metal doped and undoped polymer films remains practically the same. XPS data of PPQ-metal chloride films are listed in Table 6. A binding energy of 856.9 eV for Ni_{2p_{3/2}} and 399.3 eV for N_{1s} indicates that nickel continues to be bound to chloride in PPQ-NiCl₂. Similar result is obtained for incorporating FeCl₃·6H₂O and CrCl₃ into PPQ. The N_{1s} binding energy of PPQ-CuCl₂ and PPQ-ZnCl₂ are 400.1 eV and 400.7 eV which are

Table 5 Mechanical properties of PPQ-metal chloride films

PPQ-metal chloride film	Tensile modulus (kg/cm ²)		Elongation(%)	
	RT	200°C	RT	200°C
PPQ alone	24863	11224	29	33
PPQ-FeCl ₃	26378	12653	7	15
PPQ-NiCl ₂	27641	14184	15	72
PPQ-CuCl ₂	30144	13878	11	30
PPQ-ZnCl ₂	33984	14286	7	12
PPQ-CrCl ₃	28783	—	6	—

Table 6 XPS data of PPQ-metal chloride films

PPQ-metal chloride film	N _{1s}	M _{2p_{3/2}}
	(eV)	(eV)
PPQ alone	399.3	—
PPQ-FeCl ₃	399.3	712.3
FeCl ₃ ·6H ₂ O	—	713.1
PPQ-NiCl ₂	399.3	856.9
NiCl ₂	—	856.8
PPQ-CuCl ₂	400.1	933.5
CuCl ₂	—	936.1
PPQ-ZnCl ₂	400.7	1023.1
ZnCl ₂	—	1023.5
PPQ-CrCl ₃	399.2	578.0
CrCl ₃ ·6H ₂ O	—	578.2

higher than that of PPQ while the $\text{Cu}_{2p_{3/2}}$ or $\text{Zn}_{2p_{3/2}}$ binding energy of PPQ-CuCl₂ or PPQ-ZnCl₂ is slightly lower than that of CuCl₂ or ZnCl₂. This means that these differences are due to the partial transfer of lone-pair electrons of nitrogen atoms in PPQ to the Cu^{2+} , Zn^{2+} in CuCl₂, ZnCl₂ respectively.

In summary, metal chlorides that do not dissolve in TCE can be incorporated into PPQ by a new mixed solvent method. High-quality, flexible, glass-cast metal-containing PPQ films have been obtained. Metal-containing PPQ films exhibit improved properties in comparison with the undoped one. In the case of NiCl₂ or ZnCl₂ doping does not cause any loss in thermal stability and change in electrical resistivity. These films show increased mechanical strength and moduli at higher temperature.

Keywords:

Polyphenylquinoxaline; Metal chlorides; Incorporation; High temperature property; Mixed solvent

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