# Electrical Properties and Structural Characterizations of Polyphenylquinoxaline Pyrolyzed at High Temperature

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**ABSTRACT:** Insulating polyphenylquinoxaline (PPQ) was converted into an electrical conductor by pyrolysis at high temperature in nitrogen. Room temperature conductivity was measured as a function of pyrolytic conditions, and it was found that it strongly depends on the pyrolytic temperature and time. A maximum of room temperature conductivity about 177 S $cm^{-1}$ for PPQ film pyrolyzed at 1200°C for 1 h was obtained, which is 18 orders of magnitude greater than that of the original PPQ film. The current voltage (I–V) curve of pyrolyzed PPQ films follows Ohm's law characteristics of metals. Anisotropy in conductivity along and perpendicular to the surface of the film indicates the formation of a graphite-like structure in pyrolyzed PPQ films. The structure of the pyrolyzed PPQ films was investigated by elemental analysis, X-ray photoelectron spectroscopy spectra, X-ray diffraction, and scanning electron microscopic image. The electrical property and the structural characterizations suggest that the pyrolysis of PPQ films consists of two processes (i.e., carbonization and graphitization), and the critical temperature is at about 800°C. During carbonization ($T_p < 800$°C), some H, N, and O atoms are removed and the temperature dependence of conductivity of pyrolyzed PPQ film can be expressed by the three-dimensional Variable-Range Hopping (3-D VRH) model. During graphitization ($T_p > 800$°C), most H, N, and O atoms are removed from the residue, and a polyconjugated structure forms in it. The temperature dependence of conductivity deviates somewhat from the 3-D VRH model and can be fitted with a modified 3-D VRH model. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 69: 123–128, 1998

**Key words:** polyphenylquinoxalione, pyrolysis, electrical conductor

## INTRODUCTION

After the electrical conductivity of polyacetylene was first reported in 1977, electrically conducting polymers have been developed rapidly. Most work concentrated on several kinds of polymers possessing rigid, planar, ladder, or stepladder chain structure. These polymers can be converted into conducting materials by chemical or electrochemical oxidation or by reduction during doping.[1,2]

Polyphenylquinoxaline (PPQ) is a stepladder polymer and exhibits good thermal stability, electrical insulation, and chemical resistance. It also possesses good processing characteristics[3,4] and has unique applications in the aerospace and electionic industries. Zhang and colleagues[5] first reported the preparation of conducting PPQ in solution by means of potentiostatic oxidation, and the conductivity of conducting PPQ shows that it can be transformed into a conductor by doping. Zhou and colleagues[6] obtained conducting PPQ film by treating PPQ film in concentrated $H_2SO_4$, and the maximum value of conductivity was $10^{-2}$ S $cm^{-1}$.

Doping is an effective method to prepare conducting polymers. But, after doping, only a localized state—such as solition, polaron, and bipo-

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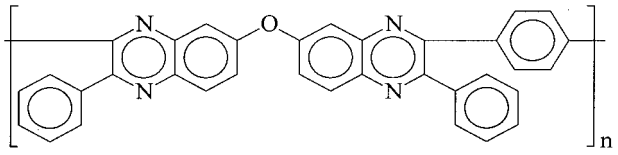

**Figure 1** Structure of PPQ.

laron—is introduced into the band-gap of polymers; the band-gap is not changed. It has attracted more interest by pyrolysis to prepare conducting materials. There have been some successful examples, such as poly[*N*,*N*′-(*p*,*p*-oxydiphenylene) pyromellitimide] (Kapton H),[7,8] poly(*p*-phenylene-1,3,4-oxadiazole),[9,10] poly(bisbenzimidazobenzophenanthroline),[11,12] and the reason is demonstrated to be due to the formation of graphite-like structure in pyrolysate. As we know, graphite is a typical organic conductor with low band-gap, so there is reason to believe that pyrolysis may be an effective method to obtain new types of materials with high conductivity and low band-gap. PPQ, as shown in Figure 1, has an aromatic heterocyclic structure with two fused fings. This feature may help form a graphite-like structure (i.e., to be turned into a conductor). Experimental results indicate that PPQ film can be converted into a conductor with conductivity, depending on pyrolytic conditions. A maximum of room temperature conductivity as high as 177 S $cm^{-1}$ for PPQ film pyrolyzed at 1200°C in nitrogen for 1 h was obtained, which is 18 orders of magnitude higher than that of the original PPQ film. It is also observed that the pyrolysis process consists of two different processes: carbonization at a pyrolytic temperature below 800°C and graphitization at above 800°C.

In this article, the effect of pyrolysis conditions, such as pyrolysis temperature and time, on the room temperature conductivity of pyrolyzed PPQ film was investigated, and its conducting mechanism and the pyrolytic mechanism are discussed.

## EXPERIMENTAL

### Preparation of PPQ Film

PPQ was prepared by polycondensation of aromatic tetraamine with aromatic dibenzil in cresol. PPQ film was obtained by casting on a glass plate, followed by complete cyclization.[3] The final product was yellow.

### Pyrolysis of PPQ Film

Pyrolysis was performed in a tube-type electrical oven and below the maximum temperature of 1300°C. PPQ films sandwiched between two quartz plates were heat-treated in the oven under a slow flow of nitrogen for a predetermined time at a pyrolytic temperature from 700 to 1200°C. The color of the film became lustrous black after pyrolysis.

### Electrical Conduction Measurements

Conductivity of pyrolyzed PPQ films was measured by the traditional four-probe method using a Keithley 196 SYSTEM DMM Digital Multimeter with ADVANTEST R6142 Programmable DC Voltage/Current Generator as a current source. Temperature dependence of their conductivity was measured at 77–300 K.

### Structure Characterizations

X-ray photoelectron spectroscopy spectra were performed on an ES 300 X-ray Photoelectron Spectrometer, using a magnesium target X-ray source. Crystallography of the pyrolyzed film was measured using a MXP 18A-HF X-ray diffractometer with a copper target ($\lambda$ = 1.5405 Å). An image of pyrolyzed PPQ film was examined by a Hitachi S-530 Scanning Electron Microscope.

## RESULTS AND DISCUSSION

### Electrical Properties

Conductivity of pyrolyzed PPQ films strongly depends on the pyrolytic conditions, such as pyrolytic temperature and time. Figure 2 shows the variation of room temperature conductivity ($\sigma_{RT}$) of pyrolyzed PPQ films at various pyrolytic temperatures ($T_p$) with pyrolytic time ($t_p$). For a given $T_p$, there are two stages of $\sigma_{RT}$ with $t_p$. At the early stage of pyrolysis, $\sigma_{RT}$ increases markedly and then tends to a saturated value with further heat treatment. The time at the point of transition between two stages is called transitional time ($t_c$). For a different $T_p$, it shows the same behavior of dependence of $t_p$ on $\sigma_{RT}$ for pyrolyzed PPQ film, but with a different $t_c$ and a maximum $\sigma_{RT}$. Figure 3 shows the relationship between $t_c$ and $T_p$, where $t_c$ drops drastically with increasing $T_p$ at low $T_p$, and then changes slowly at a higher $T_p$. A transitional temperature ($T_c$)

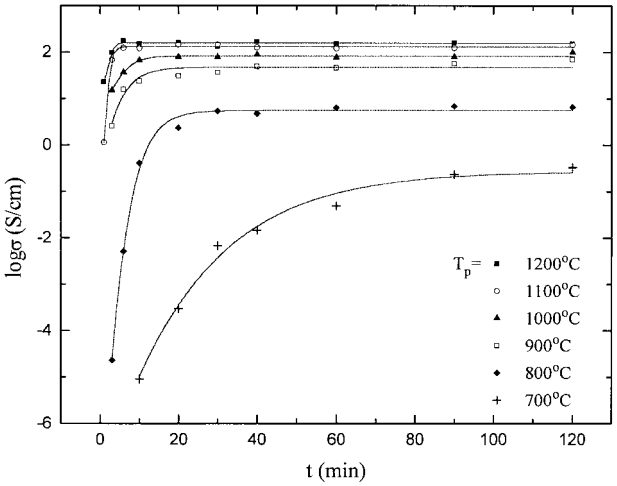


**Figure 2** Pyrolytic time dependence of PPQ films pyrolyzed at various temperatures.

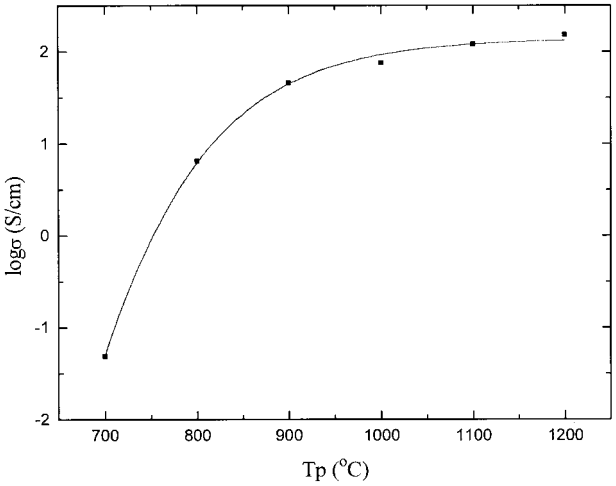


**Figure 4** Dependence of pyrolytic temperature on room temperature conductivity of PPQ film pyrolyzed for 1 h.

was estimated to be about 800°C, based on results shown in Figure 3.

The effect of $T_p$ on $\sigma_{RT}$ for PPQ films pyrolyzed for 1 h is shown in Figure 4. With increasing $T_p$, $\sigma_{RT}$ increases rapidly at low $T_p$ and tends to a constant at high $T_p$. A maximum value as high as 177 S cm$^{-1}$ for a PPQ film pyrolyzed at 1200°C for 1 h was obtained under our conditions, which is enhanced by 18 orders of magnitude, compared with the original PPQ film. Also, a transitional temperature of about 800°C was estimated from Figure 4, which is consistent with the result obtained from Figure 3. We have expressed the $T_c$ as the critical temperature of two pyrolytic processes: for $T_p < 800$°C, it is a carbonization process; and for $T_p > 800$°C, it is mainly a graphitization process.[13]

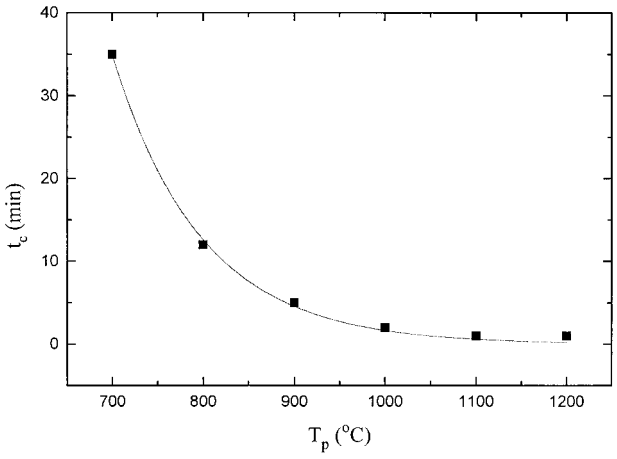


**Figure 3** Variation of critical time with pyrolytic temperature.

The results described previously indicate that the conductivity of pyrolyzed PPQ films is in the range of metal. The I–V curves of pyrolyzed PPQ films, as shown in Fig. 5, show good linear relationship, which coincide with Ohm's law—one of the typical characteristics of metals.

The temperature dependence of conductivity of PPQ films pyrolyzed at various temperatures for 1 h was measured. Results are shown in Figure 6. For the case of carbonization ($T_p = 800$°C), this relation can be explained on the basis of the three-dimensional Variable-Range Hopping (3D-VRH) model.[14] For the case in graphitization (e.g. $T_p = 1200$°C), there is a little deviation and can be fitted by $\ln \sigma T^{1/2} \sim T^{-1/4}$. Thus, the electrical conducting mechanisms are similar to that of the semiconductor.

$$\sigma(T)T^{1/2} = \sigma_0 \exp\{-(T_0/T)^{1/4}\}$$

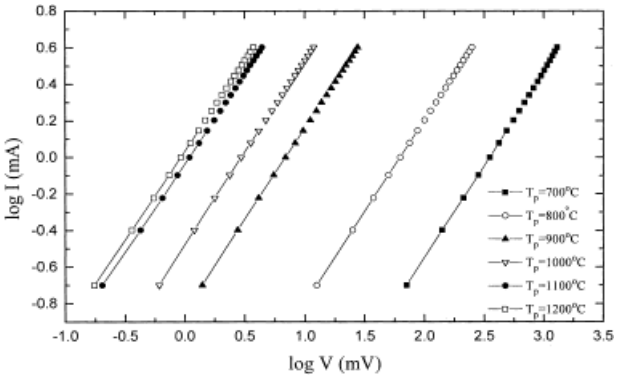


**Figure 5** I–V curve of PPQ films pyrolyzed at various temperatures for 1 h.

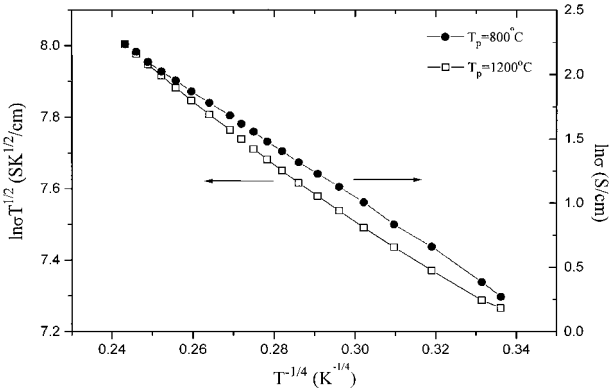


**Figure 6** Temperature dependence of conductivity of PPQ films pyrolyzed at different temperatures for 1 h.

In addition, pyrolyzed PPQ films exhibit obvious anisotropy in conductivity. For PPQ film pyrolyzed at 1200°C for 1 h, conductivity along the surface of pyrolyzed films, $\sigma\|$, which was measured by a four-probe method, is 177 S $cm^{-1}$ and that perpendicular to the surface, $\sigma\perp$, which was measured by the two-probe method, is 0.273 S $cm^{-1}$. $\sigma\|$ is 650 times greater than $\sigma\perp$. This result may be due to a graphite-like structure formed in pyrolyzed PPQ films.

### Structure Characterizations

The result of elemental analysis of the pyrolyzed PPQ films, as well as that of the original polymer, is listed in Table I. After pyrolysis at 800°C for 1 h, most of the hydrogen and some of the oxygen were removed from the polymer, and most of the nitrogen remained in the residue. After pyrolysis at 1200°C for 1 h, most of the hydrogen, oxygen, and nitrogen were removed. Ninety-seven percent of the residue is carbon, which indicates that large aromatic heterocyclic rings (i.e., graphite-like structure) formed in the pyrolysate of PPQ films.

**Table I Elemental Analysis of PPQ Films Pyrolyzed at Differnt Temperatures for 1 H**

| Sample | C (%) | H (%) | N (%) | O (%) |
|---|---|---|---|---|
| Original PPQ | 80.66 | 4.12 | 10.71 | 4.06 |
| Pyrolyzed at 800°C | 85.24 | 1.01 | 8.54 | 2.48 |
| Pyrolyzed at 1200°C | 97.11 | 0.41 | 0.86 | 0.52 |

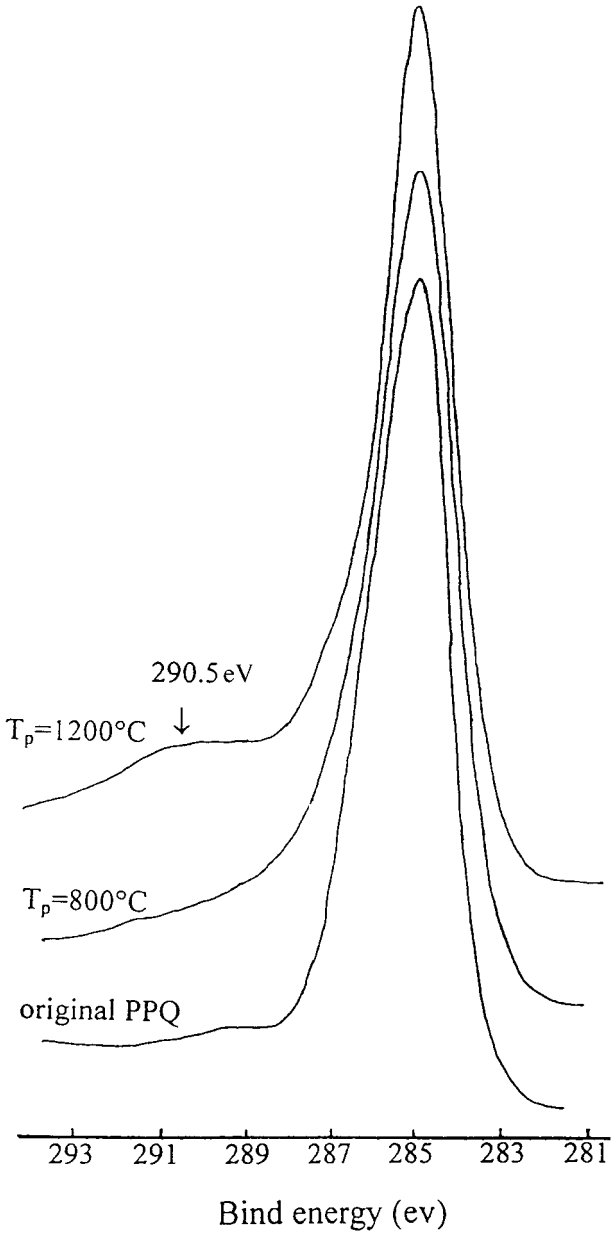


**Figure 7** $C_{1S}$ spectra of PPQ films pyrolyzed at different temperatures.

Figures 7 and 8 are the X-ray photoelectron spectroscopy of PPQ films before and after pyrolysis. Figure 7 is the $C_{1S}$ spectrum. After pyrolysis at 800°C a shakeup peak at about 289.5 eV emerged, which is due to the formation of a polyconjugated structure. After pyrolysis at 1200°C, this peak is more obvious and the position is shifted to 290.5 eV because of the formation of a more polyconjugated structure and the removal of nitrogen and oxygen atoms. Figure 8 is the $N_{1S}$ of PPQ films.

There is a peak at 399.2 eV for the original PPQ film. After being pyrolyzed at 800°C, another peak emerged at 401.2 eV with almost the same concentration as the former. After 1200°C, $N_{1S}$ signal is very weak and cannot be separated from noise, which indicates that the concentrate of the nitrogen atom is very low. The change of $O_{1S}$ is the same as that of $N_{1S}$. This result is coincident with that obtained from elemental analysis and similar to that of DEDA-DAB and PMDA-TADPE.[15]

X-ray scattering patterns of the PPQ films at different pyrolytic temperatures are shown in Figure 9. The shape of the peaks indicates that even up to 1200°C, the residue is still composed of armophous structure. For $T_p$ = 800°C, the position of the peak is changed from 4.58 Å to 3.98 Å. For $T_p$ = 1200°C, there is no further change, which indicates that structure of pyrolyzed PPQ films is disordered.

From the discussion herein, we can see that, after pyrolysis, the large plane graphite-like structure formed in pyrolyzed PPQ films, which caused great enhancement of the conductivity and anisotropy in the conductivity of PPQ films.

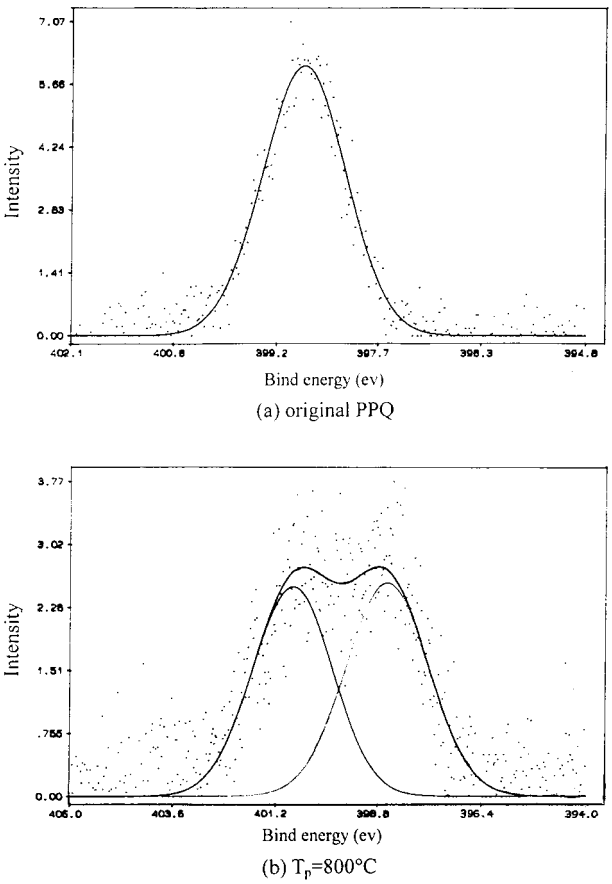


**Figure 8** $N_{1S}$ spectra of PPQ films pyrolyzed at different temperatures. (a) Original PPQ. (b) $T_p$ = 800°C.

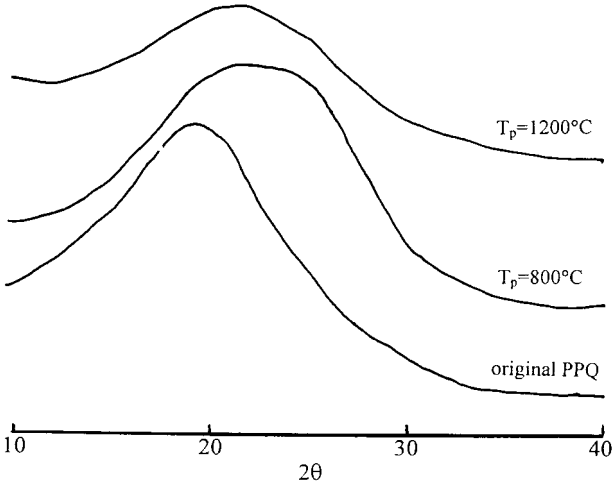


**Figure 9** X-ray scattering patterns of PPQ films at different temperatures.

## CONCLUSIONS

Pyrolysis is an effective method to convert PPQ films into conductors. Room temperature conductivities strongly depend on pyrolytic conditions, such as pyrolytic time and temperature. Pyrolysis of PPQ films consists of two processes (i.e., carbonization and graphitization), and the critical temperature of these two processes is about 800°C. Temperature dependence of conductivities of pyrolyzed PPQ films indicates that the conducting mechanism of these two processes are different and can be explained by Mott's three-dimensional Variable-Range Hopping model. Structure characterizations indicate that graphite-like structure formed in the pyrolysate of PPQ films.

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