

Preparation of Plasma-Polymerized 3-Quinolinecarbonitrile and Its Photo(electro)-Luminescence Properties

Xiong-Yan Zhao

College of Material Science and Engineering, Hebei University of Science and Technology, 050018 Shijiazhuang, People's Republic of China

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ABSTRACT: A novel plasma-polymerized 3-quinolinecarbonitrile (PP3QCN) thin film was prepared by plasma polymerization of 3-quinolinecarbonitrile (3QCN) for the first time. The PP3QCN thin films show a blue emission with a narrow peak at ~ 475 nm and there appeared a relatively high intensity of PL peak. The EL devices with PP3QCN as electroluminescent layer sandwiched between ITO and Al were fabricated. It was found that the ITO/PP3QCN/Al devices also show a blue emission and PP3QCN thin film was stable and appropriate for

the electroluminescent layer. The external quantum efficiency of ITO/PP3QCN/Al devices can reach to 0.0068%. The plasma-polymerized conjugated polynitrile thin film obtained from 3QCN precursor might be a promising material for application in LED and photodiode device. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 112: 1858–1862, 2009

Key words: polymer synthesis; plasma polymerization; 3-quinolinecarbonitrile; polynitrile

INTRODUCTION

Development of new π -conjugated polymers with high conjugation lengths and degree of interchain order are being a possible strategy to attain better materials for light emitting diode (LED) and photodiode applications.¹ In recent years, the use of π -conjugated polymers and oligomers stimulated wide interests for molecular photonic, electronic, and electroluminescent devices.^{2–4} The interesting optical properties of plasma-polymerized thin films critically depend on the conformation of the π -conjugated chains in both the ground and the excited states and on the interchain orientation. Several recent reports demonstrate that chain structures exert a considerable effect on the nature and radiative properties of excited states in π -conjugated polymers.⁵ Plasma polymerization is gaining recognition as an important technique for direct film deposition of entirely new kinds of polymeric materials, which are hard to obtain by the conventional polymerization methods. Moreover, the films obtained by plasma polymerization are generally of high quality,

homogeneous, adherent, and pinhole free films.^{6,7} Controllability and reproducibility of the surface composition of plasma deposition thin film are utmost important to achieve superlative performance. Also, it is well known that several plasma reaction parameters like power input, monomer flow rate, and substrate temperature influence the structure and the composition of plasma thin films.^{8,9} And it is now recognized that under low discharge power input conditions, a plasma-deposited polymer is created that retains more of the aromatic ring structures of the starting monomer and resembles a more conventional polymer.^{10–12}

To our knowledge, no reports have yet been made concerning the study of poly(3-quinolinecarbonitrile). In the present work, the technique of plasma polymerization was used in the preparation of plasma-polymerized conjugated poly(3-quinolinecarbonitrile) thin film. Scheme 1 shows the monomer 3QCN structure and the desired structure of plasma-polymerized 3-quinolinecarbonitrile (PP3QCN). The body of this article will focus on performing preparation and analysis of structural and photoluminescence and electroluminescence properties of PP3QCN thin film.

EXPERIMENTAL

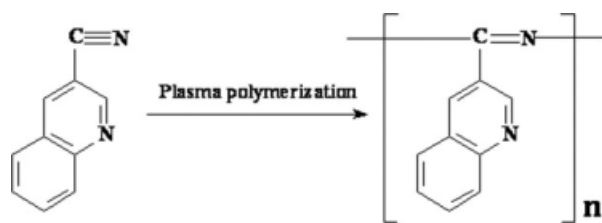
Materials

3-quinolinecarbonitrile (3QCN, >98%) was purchased from Aldrich Chemical Company and was used without any further purification. The nitrogen

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Scheme 1 Chemical structure of monomer 3QCNC, and the desired structure of plasma-polymerized conjugated polynitrile PP3QCNC.

and argon used in the plasma system was high-purified grade.

Substrate cleaning

The quartz substrates used in plasma polymerization were cleaned consecutively three times. The substrates were first base cleaned for 15 min at 70°C on a hot plate in a mixture of 25 mL of 30% NH_4OH , 25 mL of 30% H_2O_2 , and 125 mL of deionized water. After rinsing with deionized water, the substrates were then acid cleaned for 15 min at 70°C on a hot plate in a mixture of 25 mL of HCl , 25 mL of 30% H_2O_2 , and 125 mL of deionized water. The cleaned substrates were next rinsed with deionized water and then were kept in the vacuum oven for 24 h at 120°C for drying. Finally, the substrates were put into plasma chamber and cleaned with argon plasma (80 W) for 3 min just before plasma polymerization.

Plasma polymerization

Plasma polymerization of 3QCNC was carried out using a radiofrequency (13.56 MHz) capacitive coupled glow discharge system. A cylinder-shaped stainless steel plasma polymerization reactor was fitted with parallel plate electrodes. The substrates were centered on the bottom electrode, after evacuation and purging with high purity nitrogen three times, the RF system was adjusted to powers selected and a glow discharge was allowed to occur for fixed times. The pressure of the reaction chamber was maintained at about 45 mTorr during the glow discharge. After the plasma was extinguished, the high purity nitrogen was induced to the chamber until the pressure of reactor became more than 2 Torr, after which the reactor was brought to atmospheric pressure with air. The plasma thin films deposited directly onto quartz substrate were used in the characterization of UV-Vis, PL, XPS and the measurements of film thickness, and whereas the plasma thin films deposited onto potassium bromide (KBr) pellet was used only for FT-IR analysis. For the EL measurements, the PP3QCNC films were deposited on ITO glasses, after then the cathode alumi-

num was coated by evaporating high-purity aluminum wire under the high vacuum.

Measurements

The film thickness was measured using a surface profiler (α -Step 500). The UV-Vis absorption spectra were recorded using a UV-Vis recording spectrophotometer (Shimadzu, Model UV-2501PC). The FT-IR spectra were measured on a Perkin-Elmer System 2000 FT-IR spectrometer. An X-ray photoelectron spectrometer (Kratos, Axis ULTRA) was used for XPS measurements with an Al $\text{K}\alpha$ X-ray source. Fluorescence measurements were conducted on a Shimadzu RF5000 spectrofluorophotometer. Thermal stability measurements were carried out on a Hi-Res TGA 2950 thermogravimetric analyzer under a nitrogen flow at a heating rate of 10°C/min.

RESULTS AND DISCUSSION

The thickness of PP3QCNC thin film was measured as a function of deposition time. As shown in Figure 1, a linear increase in film thickness with deposition time is observed for the PP3QCNC thin film. It should be pointed out that the plotted values are the average thickness taken from four positions of the bottom electrode. The slope of the linear curve can give the deposition rate of the plasma thin films. The deposition rate of monomer 3QCNC was found to be 55.84 nm/min when the discharge power was 10 W.

Figure 2 illustrates the UV-vis absorption spectra of PP3QCNC thin film and its monomer 3QCNC. It has been reported that the pure 3QCNC shows an absorption band at about 235 nm (see inset), which can be attributed to the π - π^* transition of the 3QCNC aromatic ring. In comparison with the monomer absorption band, the maximum absorption wavelength (λ_{max}) of PP3QCNC thin film shows an obvious red

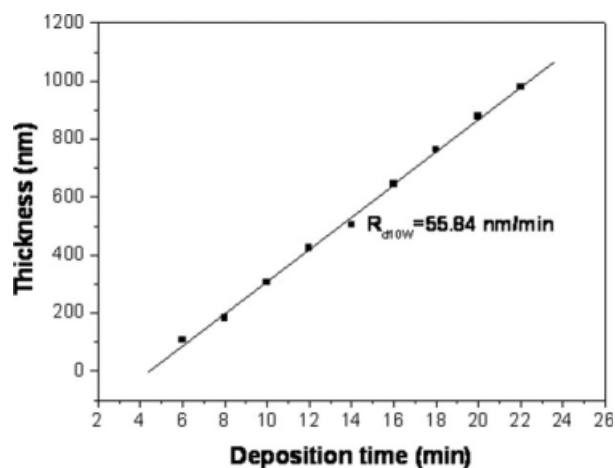


Figure 1 Thickness of films as a function of deposition time at discharge power of 10 W.

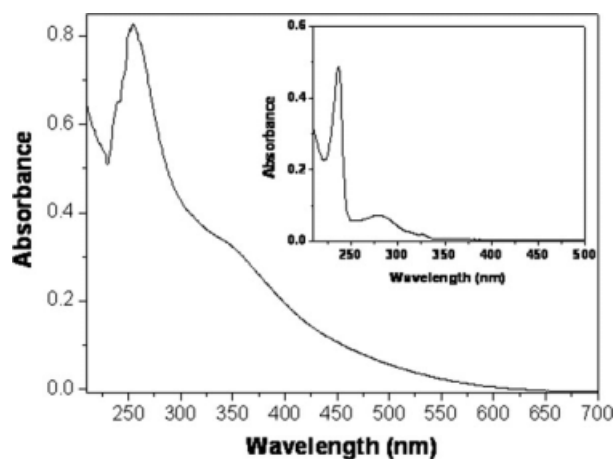


Figure 2 UV-Vis absorption spectra of PP3QCN. Inset: UV-Vis absorption spectrum of the starting monomer 3QCN.

shift, the maximum of red shift of more than 20 nm (257 nm vs. 235 nm) is observed. Moreover, the width of absorption band for PP3QCN thin film was also found to increase obviously as compared with that of monomer 3QCN. It is well known that increasing the length of the conjugated π -system generally moves the absorption maximum to longer wavelengths.¹³ Appearing a red shift and wider peak width indicate that a larger conjugated π -system has been formed in PP3QCN thin film during the plasma polymerization of 3QCN. Clearly, a higher retention of the aromatic ring structure of the starting monomer in the deposited plasma films is obtained under the low plasma discharge power of 10 W.

The FT-IR spectra of monomer 3QCN and PP3QCN thin film are shown in Figure 3 as curves a and b, respectively. Clearly, there is a very strong absorption band at 2230/cm for monomer 3QCN, which is ascribable to the $C\equiv N$ stretching vibration.

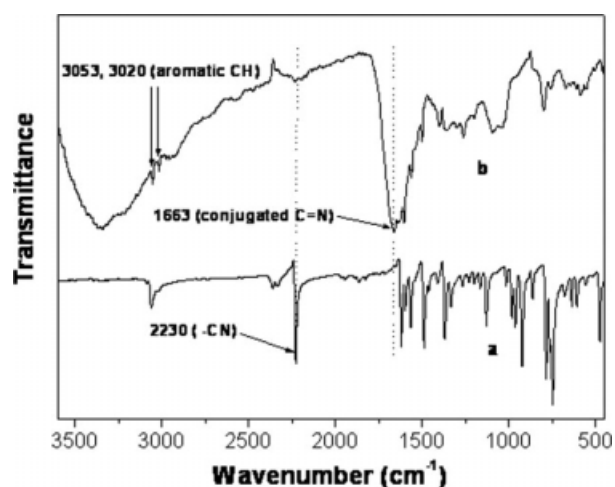


Figure 3 FTIR spectra of (a) 3QCN and (b) PP3QCN film.

However, this absorption band no longer existed for the plasma PP3QCN thin film. Instead, there appeared a broader and considerably stronger absorption band at 1663/cm for the plasma PP3QCN film, attributed to the conjugated $C=N$ stretching vibration, which indicated that extensively conjugated $C=N$ double bonds were formed during the plasma polymerization of 3QCN through the opening of $C\equiv N$ triple bonds. Moreover, it is also clear that the characteristic absorption bands at 3020 and 3053/cm for the aromatic $C-H$ stretching vibration have been preserved to a large extent for the PP3QCN thin film. This suggests that most of the aromatic ring structures of starting monomers are preserved for deposition carried out at the power of 10 W, which is also confirmed by the prominent characteristic absorption bands at 1604, 1555, 1501, and 1410/cm of the aromatic ring backbone stretching vibrations. The above observations agree well with the UV-vis results.

To get the detailed surface stoichiometry of plasma conjugated polynitrile thin films, the high-resolution C 1s spectra of PP3QCN film were evaluated and the corresponding results are shown in Figure 4. It has been reported that the full width at half maximum (FWHM) for plasma polymers is expected to be relatively large, about 2 eV because of their irregular molecular structure.^{14,15} Thus, the C 1s spectra for PP3QCN film were curve-fitted using 2 eV as the FWHM. It should be noted that some fitting peaks significantly overlap because of the small difference in the binding energies associated with these peaks. The C 1s spectra of PP3QCN film can be deconvoluted into five component peaks as indicated in Figure 4. The binding energy for aromatic $C=N$ (285.97 eV) and $C=C$ (285.47 eV) was assigned in accordance with the results in the literature¹⁶ and the peak positions for both aromatic components were fixed during the fit procedure. The other three chemically distinct C atoms are assigned as follows: the peak at

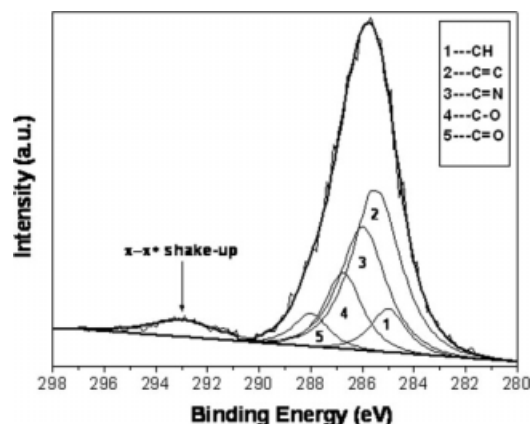


Figure 4 C 1s spectra of PP3QCN film.

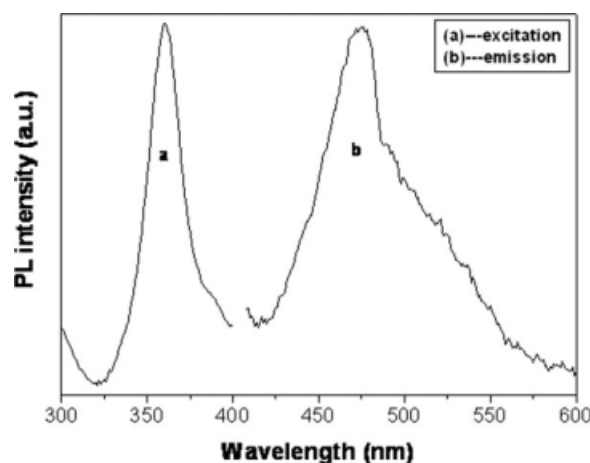


Figure 5 Photoluminescence spectrum of PP3QCN thin film.

284.90 eV represents saturated hydrocarbon CH; the peak at 286.75 eV represents the C—O group; and the peak at 288.04 eV represents C=O. In addition, a broad high binding energy peak centered at 292.88 eV, which assigned to the π - π^* shake-up satellite arising from the aromatic rings is observed for PP3QCN thin film, indicating that the PP3QCN film contains an extended π -electron system. In other words, a higher retention of the aromatic ring structure in the PP3QCN film is obtained during the plasma polymerization of 3QCN. The theoretical ratio of the group C=N to C=C in PP3QCN film is 1 : 2 if plasma polymerization occurred exclusively through the C \equiv N triple bond. For the PP3QCN film deposited at 10 W, this ratio is 1 : 2.25.

The PL spectrum of the as-grown PP3QCN is shown in Figure 5. It can be seen from the spectrum that the as-grown plasma PP3QCN thin film show a blue emission with a narrow peak at \sim 475 nm and there appeared a relatively high emission intensity of PL peak. Clarkson and coworkers¹⁷ reported the preparation and optical property of plasma-polymerized benzene and furan films and found that photoluminescence spectra of these films show a blue emission with a broad peak at 460 nm for the plasma-polymerized benzene films and 445 nm for the plasma-polymerized furan films, which are different from our results with a narrow emission peak. This discrepancy is probably due to difference in structures of plasma polymer thin films studied. Generally speaking, the optical property of organic materials was influenced by the nature of the lowest electronic excited states. Because of the strong electron–phonon coupling, the optical property of highly conjugated plasma polymer thin films was influenced by both the ground and excited state equilibrium conformation of the resulting molecules. It has been reported¹⁸ that the emission with a narrow transition and a high PL intensity mainly arises from

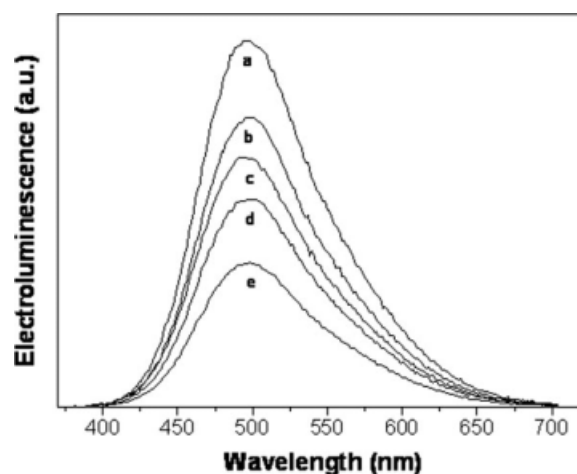


Figure 6 The EL spectra of the ITO/PP3QCN/Al devices fabricated with different PP3QCN layer thicknesses: (a) 305.2 nm; (b) 183.8 nm; (c) 108.2 nm; (d) 425.1 nm; and (e) 505 nm.

the crystalline parts. In this research, therefore, the narrow blue emission with a high intensity of PL peak might mainly originate from the crystalline structures formed in conjugated PP3QCN film during plasma polymerization. Indeed, it was found by Boo and coworkers¹⁹ through study on the optical behaviors of plasma-polymerized thiophene that there was an existence of some crystalline structures in plasma-polymerized thiophene films.

The EL spectra of the ITO/PP3QCN/Al devices with different PP3QCN layer thickness are illustrated in Figure 6 as curves a, b, c, d, and e. It is clear that all the EL spectra shapes are similar to each other and they show a blue emission as its PL spectra. Furthermore, the FWHM for all the EL spectra as a whole is about 95 nm. Sun et al.²⁰ reported the preparation and EL property of plasma-polymerized naphthalene (PPN) and found that the FWHM

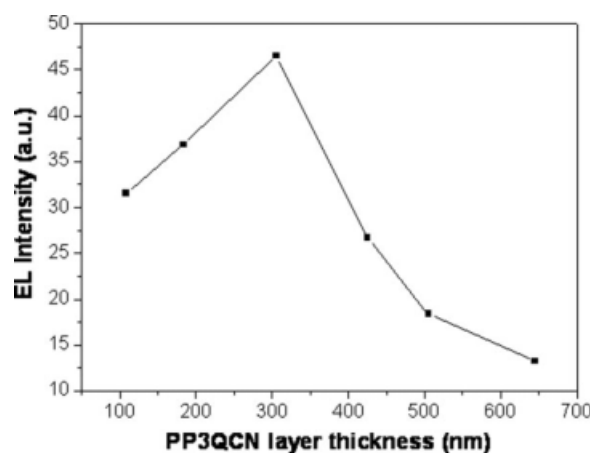


Figure 7 The relationship between EL intensity of the ITO/PP3QCN/Al devices and PP3QCN layer thicknesses under a constant current.

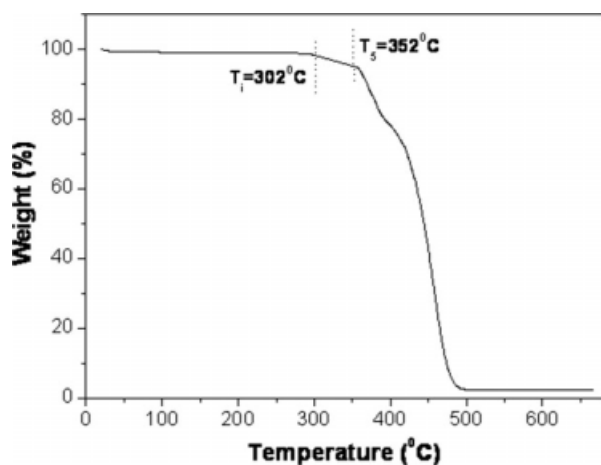


Figure 8 TGA thermogram of PP3QCN sample.

of PPN EL device is 100 nm, which is similar to our results. Seoul and Song²¹ also investigated the EL property of polymer light-emitting devices based on PPN, and the FWHM of EL spectrum of PPN device was found to be 180 nm, they believe that the difference in FWHM comes from the structural differences, resulting from the plasma polymerization apparatus and conditions. The effects of PP3QCN layer thickness on EL intensity are shown in Figure 7. It can be seen that there is an optimal thickness for ITO/PP3QCN/Al devices; the optimum thickness is about 305 nm. For the ITO/PP3QCN/Al devices fabricated with a polymer layer thickness of 305 nm, the EL quantum efficiency was 0.0068%.

The stability of light emitting polymers is essential for their potential applications in the field of EL devices because impurities formed during heating generally serve as quenching sites for excitons. The polymers lose their emitting qualities on heating while showing rather small changes in the electronic absorption spectra. There can be oxidation reactions on heating, which produces carbonyl groups in the molecules. There are very effective exciton quenching sites. To determine the thermal behavior of plasma-conjugated PP3QCN sample, TGA analysis of PP3QCN was carried out at a scanning rate of 10°C/min. The results are shown in Figure 8. It is clear that the onset of degradation temperature of PP3QCN sample occurred at 302°C and the decomposition temperature at 5% weight loss occurred at 352°C. The better thermal behavior of PP3QCN sample can be attributed to a higher retention of the aromatic ring structure in the PP3QCN sample. It has been recognized that^{10,12} under low discharge power input conditions, a plasma-deposited polymer is created that retains more of the aromatic ring structures of the starting monomer and resembles a more conventional polymer. Furthermore, a crosslinking structure formed during the plasma polymerization

of 3QCN should be another effective factor for the formation of stable PP3QCN emitting layer. Thus, the PP3QCN is a good candidate for the EL emitting layer.

CONCLUSIONS

A novel conjugated polynitrile PP3QCN thin film with a large π -conjugated system has been prepared by the plasma polymerization technique. FT-IR, UV-Vis, and XPS studies revealed that a higher retention of the aromatic ring structure in the deposited plasma films is obtained and the plasma polymerization of 3QCN took place mainly through the opening of the π bonds of $C\equiv N$ functional group under our experimental conditions. The as-grown conjugated polynitrile thin film shows a blue emission with a relatively high PL intensity at about 475 nm. Moreover, the EL devices fabricated with PP3QCN sandwiched between ITO and Al showed a relatively stable light emitting.

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