

# Preparation of plasma poly(1-isoquinolinecarbonitrile) thin film and its ultrafast nonlinear optical property

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How to get a uniform, defect-free, and reproducible conjugated polymer thin films is now becoming the main fabrication problem for the practical application of these materials as the fast switches and modulators in opto-electronic devices. In this research, a novel plasma-polymerized 1-isoquinolinecarbonitrile (PPIQCN) thin film was prepared by plasma polymerization under different glow discharge conditions. The effect of the discharge power on the chemical structure and surface compositions of the deposited PPIQCN films was investigated by Fourier transform infrared (FTIR), UV-Visible absorption spectra and X-ray photoelectron spectroscopy (XPS). The results show that a high retention of the aromatic ring structure of the starting monomer in the deposited plasma films is obtained when a low discharge power of 10 W was used during film formation. In the case of higher discharge power of 30 W, more severe monomer molecular fragmentation can be observed, which results in a decrease in the effective conjugation length of PPIQCN film. The morphology characterized by atomic force microscopy (AFM) indicates that a fine, homogenous PPIQCN film could be obtained under a relatively low discharge power. A femtosecond time-resolved optical Kerr effect technique at a wavelength of 820 nm has been applied to investigate the third-order nonlinearity of the plasma PPIQCN film. For the first time, a non-resonant optical Kerr effect and ultrafast response of the PPIQCN film was observed.

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## 1. Introduction

Recently, special attention has been focused on conjugated organic polymers for their potential in the design and synthesis of advanced materials. The  $\pi$ -electron delocalization in conjugated polymer backbones contributes to the ultrafast response capability and large third-order nonlinearity. Conjugated polymers with efficient and fast optical response have been demonstrated to be promising materials for opto-electronic device applications. In fact, the use of  $\pi$ -conjugated polymers and oligomers stimulated wide interests for molecular photonic, electronic, and electro-luminescent devices [1–3]. Of the many conjugated polymers, polynitriles have been found to be an unusual class of polymers with good environment stability, optical transparency [4], large second-order hyperpolarizability [5] as well as excellent and reproducible

electrical bistability property [6]. However, the progress on the studies of the polynitrile polymers has been hampered due to the difficulties in synthesizing the conjugated C=N polymers [7, 8].

Plasma polymerization is gaining recognition as an important technique for direct film deposition of entirely new kinds of polymeric materials, which are hardly possible to obtain by the conventional polymerization methods, and the films obtained by plasma polymerization are generally of high quality, homogeneous, adherent, and pinhole free [9, 10]. Controllability and reproducibility of the surface composition of plasma deposition thin film is utmost important to achieve superlative performance. 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

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TABLE I Plasma polymerization conditions and film thickness

Plasma polymer	PPIQCN10	PPIQCN30
Discharge power (W)	10	30
Pressure (mTorr)	21	21
Deposition time (s)	10	10
Film thickness (nm)	352	496

films [11, 12]. And it is now recognized that under low discharge power input conditions, a plasma polymer is created that retains more of the aromatic ring structures of the starting monomer and resembles a more conventional polymer [13–15].

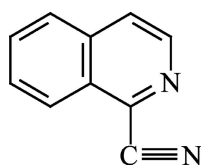
Here, we report the preparation and characterization of a novel plasma-polymerized 1-isoquinolinecarbonitrile (PPIQCN) thin film (Table I) as well as its ultrafast third-order optical nonlinearity. One of the objectives of this work is to prepare a conjugated PPIQCN thin film with a uniform and defect-free surface as well as an ultrafast NLO response property.

### 1.1. Experimental details

1-isoquinolinecarbonitrile (>98%) was purchased from Aldrich Chemical Company and was used without any further purification. Scheme 1 shows the monomer structure. The nitrogen and argon used in the plasma system were high-purified grade.

The substrates used were glass slide, quartz glass and freshly pressed FTIR-grade KBr. Before depositing the films, the substrates (except KBr) were first base cleaned for 15 min at 70°C on a hot plate in a mixture of 25 mL of 30% NH<sub>4</sub>OH, 25 mL of 30% H<sub>2</sub>O<sub>2</sub>, and 125 mL of deionized water. After rising 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<sub>2</sub>O<sub>2</sub>, 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 at a power of 80 W for 3 min just prior to plasma polymerization.

Plasma polymerization of 1-isoquinolinecarbonitrile 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 pure nitrogen for three times, the RF



Scheme 1 Chemical structure of monomer 1-isoquinolinecarbonitrile.

system was adjusted to the pre-set powers, glow discharge was allowed to occur for certain duration. The pressure of the reaction chamber was maintained at about 20–25 mTorr during the glow discharge. After the plasma was extinguished, the chamber was evacuated to 40 mTorr for 5 min, and then the high pure 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 to the characterization of UV-vis, AFM and Optical Kerr Effect (OKE), the plasma thin film deposited onto glass slide were used to the measurements of film thickness and XPS analysis while the plasma thin film deposited onto potassium bromide (KBr) pellet was used only for FT-IR analysis.

The FT-IR spectra were measured on a Perkin-Elmer System 2000 FT-IR spectrometer. Each spectrum was collected by accumulating 64 scans at a resolution of 8 cm<sup>-1</sup>. The UV-Vis absorption spectra were recorded using a UV-Vis recording spectrophotometer (Shimadzu, Model UV-2501PC). The film thickness was measured using a surface profiler (Alpha-Step 500). An X-ray photoelectron spectrometer (Kratos, Axis ULTRA) was used for XPS measurements with an Al K<sub>α</sub> X-ray source. Both low-resolution survey spectra and high-resolution core level spectra were taken for carbon, nitrogen and oxygen. The samples were not ion-sputter cleaned in the XPS chamber, as the effects of ion bombardment on the film composition and morphology were judged to be too severe. The morphology of plasma film was characterized using an atomic force microscopy (AFM) in tapping mode under a constant force (Digital Instruments, NanoScope IIIa), the roughness was obtained from the 2 × 2 μm<sup>2</sup> scan. The OKE measurements were performed using ultrashort pulses generated from a femtosecond Ti:sapphire laser. The full width at half maximum (FWHM) of laser pulse was about 120 fs at 820 nm.

## 2. Results and discussion

The FT-IR spectra of the plasma-polymerized 1-isoquinolinecarbonitrile (PPIQCN) films deposited at discharge powers of 10 W and 30 W are illustrated in Fig. 1 as curves b and c, respectively. The absorption spectrum of the 1-isoquinolinecarbonitrile monomer is shown in curve a for comparison. Clearly, there appeared a broader and considerably stronger absorption band at 1650 cm<sup>-1</sup> for both plasma PPIQCN films, attributed to the conjugated C=N stretching vibration as compared with the monomer 1-isoquinolinecarbonitrile, which indicated that extensively conjugated C=N double bonds were formed during the plasma polymerization of 1-isoquinolinecarbonitrile. It is also clear that the characteristic absorption bands at 3043 and 3096 cm<sup>-1</sup> for the aromatic C–H stretching vibration have been preserved to a large extent for the PPIQCN10 film deposited at 10 W, indicating greater retention of aromatic ring structure in PPIQCN10 film. On the other hand, however, the

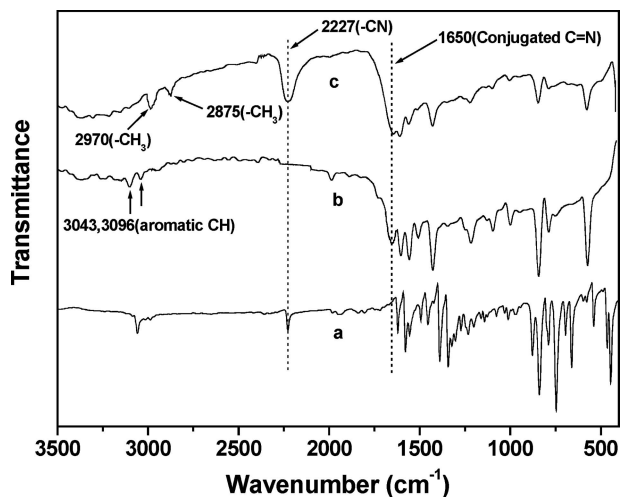


Figure 1 FTIR spectra of (a) 1-isoquinolinecarbonitrile; (b) PPIQCN10; and (c) PPIQCN30.

absorption intensity of the same absorption bands for the PPIQCN30 film has diminished significantly. This is indicative of increasing monomer fragmentation during the high power plasma polymerization. In addition, the new absorption bands appeared at  $2970\text{ cm}^{-1}$  ( $-\text{CH}_3$ ,  $\nu_{\text{as}}$  stretching vibration) and  $2875\text{ cm}^{-1}$  ( $-\text{CH}_2$ ,  $\nu_{\text{s}}$  stretching vibration) in PPIQCN30 film further confirm above deduction. Moreover, the prominent characteristic absorption bands at  $1603$ ,  $1552$ ,  $1508$ , and  $1424\text{ cm}^{-1}$  of the aromatic ring backbone stretching vibration also indicate the greater retention of aromatic ring structure in PPIQCN10 film. Thus, the FT-IR results suggest that the plasma polymerization of 1-isoquinolinecarbonitrile has proceeded mainly via the opening of  $\pi$ -bond of the  $\text{C}\equiv\text{N}$  functional groups under low discharge powers while the high power plasma polymerization gives rise to more severe molecular (aromatic ring) fragmentation. Simultaneously, we also found in Fig. 1 that the  $\text{C}\equiv\text{N}$  stretching vibration at about  $2227\text{ cm}^{-1}$  was also present in PPIQCN30 film deposited at 30 W. This can be attributed to the unreacted  $\text{C}\equiv\text{N}$  species, which split from the monomer molecule and deposited on the surface of the films during the high discharge power plasma polymerization.

Fig. 2 illustrates the UV-Vis absorption spectra of the 1-isoquinolinecarbonitrile monomer and its corresponding plasma-polymerized thin films deposited at different powers. The pure 1-isoquinolinecarbonitrile shows an absorption band at about 228 nm, which can be attributed to the  $\pi$ - $\pi^*$  transition of the aromatic 1-isoquinolinecarbonitrile ring. In comparison with the monomer absorption band, the absorption band of PPIQCN10 film turns out to be stronger and extends to the visible region, the maximum absorption wavelength ( $\lambda_{\text{max}}$ ) of PPIQCN10 film shows an obvious red shift, the maximum of red shift of more than 60 nm (292 nm vs. 228 nm) is observed. It is well known that increasing the length of the conjugated  $\pi$ -system generally moves

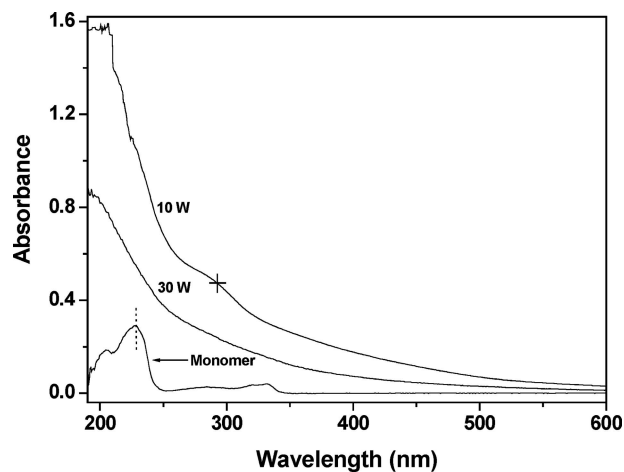


Figure 2 Effects of discharge power on UV-Vis absorption for fixed deposition duration of 10 min.

the absorption maximum to longer wavelengths [16]. So, this result indicates that a larger conjugated  $\pi$ -system has been formed in PPIQCN10 film during the polymerization of monomer 1-isoquinolinecarbonitrile. Clearly, a higher retention of the aromatic ring structure of the starting monomer in the deposited plasma films is obtained under the low discharge power plasma polymerization, which agrees well with the FT-IR results. It also can be seen from Fig. 2 that there is no any characteristic absorption appeared in PPIQCN30 film and its absorption intensity become much weaker than that of PPIQCN10 film. This indicates that the effective conjugation length of PPIQCN30 film has been diminished considerably under the higher discharge power plasma polymerization. Since, as we reported before [17], when the plasma polymerization is carried out under a higher discharge power, more aromatic rings of monomers are dissociated and fragmented, which results in more non-conjugated polymers being formed in the plasma polymerized films and this effect is become more prominent with further increasing RF power. Hence, it is not difficult to understand that the high discharge power plasma of 30 W gave rise to a decrease in the effective conjugation length of plasma-polymerized 1-isoquinolinecarbonitrile as indicated by the result shown in Fig. 2.

The survey XPS spectra reveal that besides carbon and nitrogen, there are also significant amounts of oxygen in all PPIQCN films. The presence of oxygen is normally expected in the plasma-polymerized films owing to the existence of trace oxygen adsorbed on the wall of the reaction chamber system and also due to the reaction of long-lived radicals with atmospheric oxygen after being exposed to the air. In order to check the effect of discharge power on the chemical compositions of PPIQCN films, the high-resolution C 1s spectra of plasma films deposited under different discharge powers were evaluated. The C 1s spectra were analyzed by fitting Gaussian peaks using a least squares fitting routine and the peaks were chosen to be the standard Gaussian with

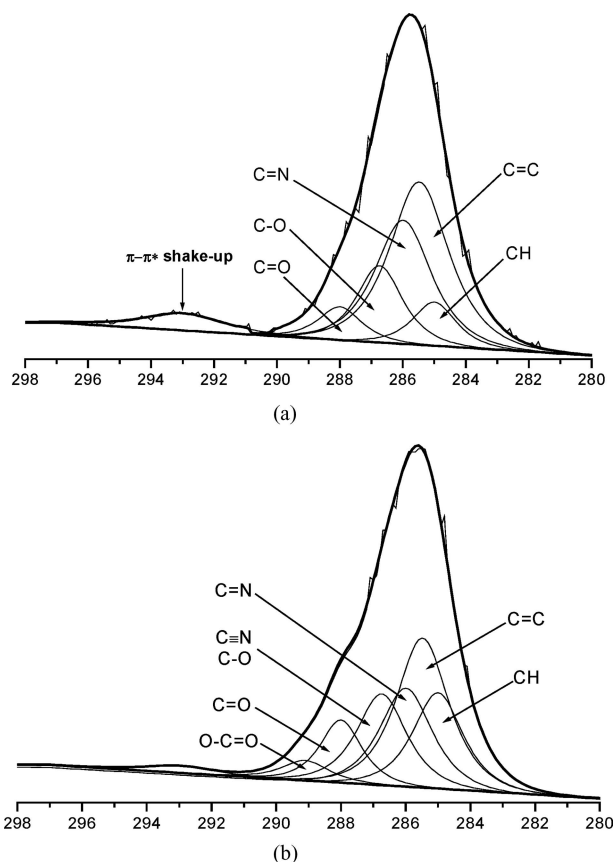


Figure 3 C 1s spectra of (a) PPIQCN10 and (b) PPIQCN30.

a 20% Lorentzian structure. It has been reported that the full width at half maximum (FWHM) for plasma polymers is expected to be relatively large, about 2 eV due to their irregular molecular structure [18, 19]. So, the C 1s spectra for all PPIQCN films were curve fit using the same fitting parameters as mentioned above. It should be noted that some fitting peaks are significant overlap due to these peaks within a small range of binding energy and also relatively broad. The C 1s spectra can be deconvoluted into six component peaks as indicated in Fig. 3. The binding energy for aromatic C=N (285.99 eV) and C=C (285.48 eV) was assigned in accordance with the results in the literature [20]. The other four chemically distinct C atoms are assigned as follows: the peak at 285.00 eV represents saturated hydrocarbon CH; the peak at 286.74 eV represents the groups such as C≡N and C-O; the peaks at 288.00 eV represents C=O; and the peaks at 289.10 eV represents O-C=O. In addition, a broad high binding energy peak centered at 293.50 eV, which assigned to the  $\pi$ - $\pi^*$  shake-up satellite arising from the aromatic rings is observed for PPIQCN10 film (Fig. 3a), indicating that the PPIQCN10 film contains an extended  $\pi$ -electron system [21]. In other words, a higher retention of the aromatic ring structure in the PPIQCN10 film is obtained under the discharge power of 10 W. For PPIQCN30 film deposited at a high discharge power of 30 W (Fig. 3b), however, the contents of aromatic C=C and C=N component in PPIQCN30 film were found to decrease substantially

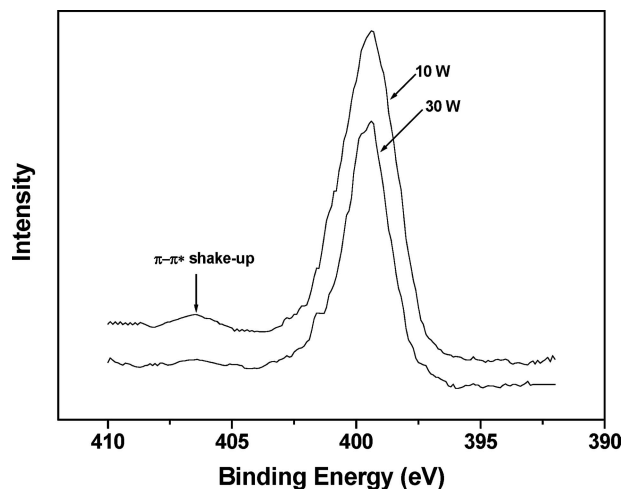


Figure 4 N 1s spectra of the plasma-polymerized 1-isoquinolinecarbonitrile films. The curve of PPIQCN10 film was shifted upward vertically.

comparing with that for the PPIQCN10 film. Meanwhile, the relatively contents for component CH, C≡N, C=O and O-C=O, formed during the plasma polymerization process, were found to increase significantly, indicating more intensive monomer fragmentation process promoted by the high discharge power of 30 W. The theoretical ratio of the group C=C to C=N in PPIQCN films is 1:0.5 if plasma polymerization occurred exclusively through the C≡N triple bond. For the PPIQCN10 film, this ratio is 1:0.35. On the other hand, for the PPIQCN30 film deposited at a higher power of 30 W, the corresponding ratio decreases to 1:0.18. Thus, it is clear that the aromatic ring structure in the PPIQCN10 film is preserved more effectively for deposition carried out at the low discharge power of 10 W. Furthermore, it is also clear from Fig. 3 that the intensity of the  $\pi$ - $\pi^*$  shake-up satellite for PPIQCN30 film is much weaker than that of the films deposited at the low discharge power, also revealing less retention of the aromatic ring structure in the PPIQCN30 film.

The significant difference in composition of the PPIQCN films for high and low discharge power probably arises from the difference in bond scission mechanism during the plasma polymerization. It has been reported [13, 22,] that at the low discharge power, the plasma polymerization mainly carries out in the energy-deficient state and the energy per unit mass of the molecule is very low. Thus, bond scission occurs mainly at the  $\pi$ -bond of the functional group C≡N, which has the lowest bond energy. Under these conditions, rearrangement of the active radicals leads to a plasma polymer having a similar chain structure to that of the conventional polymer. For a high discharge power, however, the plasma polymerization process transforms from an energy-deficient state to a more energetic state. More energy per unit mass of the monomer will result in more severe molecular fragmentation. Thus, it is not difficult to understand that under a high discharge power, plasma polymerization of



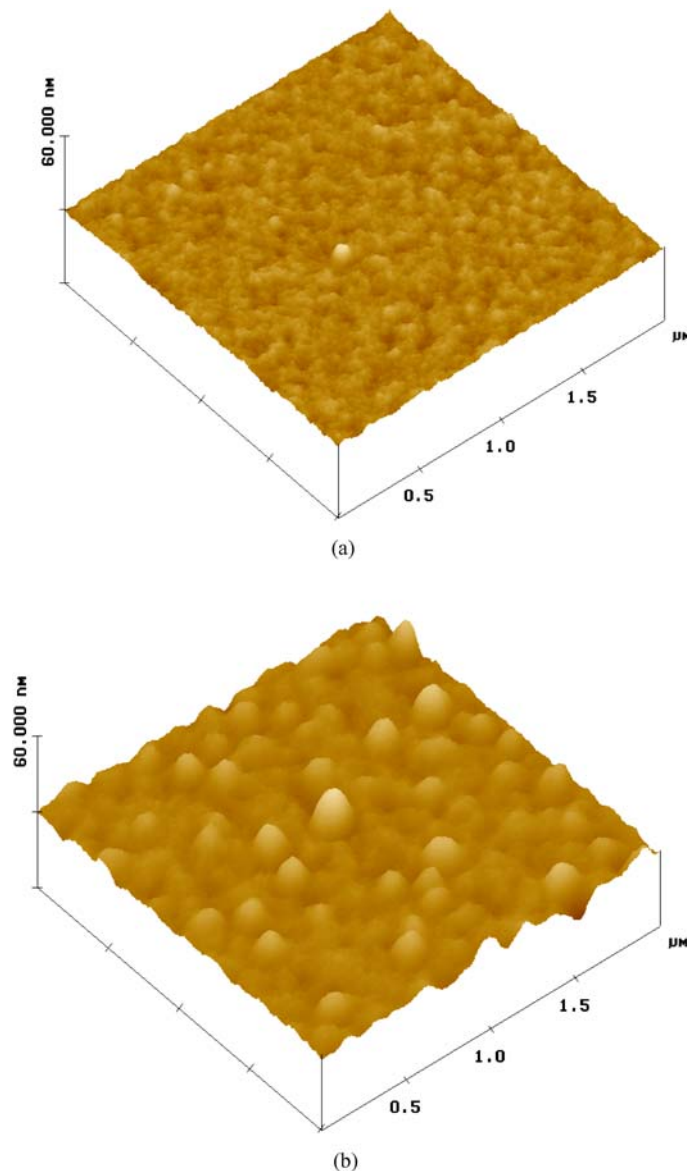


Figure 5 AFM images of (a) PPIQCN10 and (b) PPIQCN30.

1-isoquinolinecarbonitrile will produce more active radicals, which come from scissions of not only the  $\pi$ -bond of the  $C\equiv N$  functional group but also the aromatic ring. The latter reactions help to account for the decrease in contents of the aromatic species  $C=C$  and  $C=N$  and an increase in content of the aliphatic CH.

Fig. 4 shows the N 1s core-level spectra of the two PPIQCN plasma films deposited at different powers of 10 W and 30 W. Again, a broad but distinct high binding energy  $\pi-\pi^*$  satellite peak centered at 406.4 eV is observed for PPIQCN10 film, indicating greater retention of aromatic ring structures in PPIQCN10 films. The significant decrease in  $\pi-\pi^*$  satellite intensity for PPIQCN30 film suggests that much more aromatic ring structure of monomer is lost during the plasma polymerization. In addition, since the peaks arising from the component  $C=N$  (399.34 eV) and  $C\equiv N$  (399.57 eV) are too close in binding energy to distinguish, the N 1s core-level spectra only

revealed limited information about the structure of the plasma films.

The surface morphology of the PPIQCN films deposited on quartz substrate at different discharge powers was observed using AFM. The AFM images in Fig. 5 show that a high-quality PPIQCN film could be obtained under a lower discharge power of 10 W (Fig. 5a). It is transparent, homogeneous and pinhole-free, quite suitable for the measurement of nonlinear optical properties. The RMS roughness is only 0.51 nm for PPIQCN10 film. The smooth morphology suggests that the plasma polymerization has occurred predominantly on the substrate surface, instead of in the gas phase [18]. The plasma film grows through reaction with the monomer species that reach the substrate surface. On the other hand, in the case of higher discharge power such as 30 W, the PPIQCN film (Fig. 5b) has a rough surface with a RMS roughness of 2.32 nm, much larger than the low power deposited value,

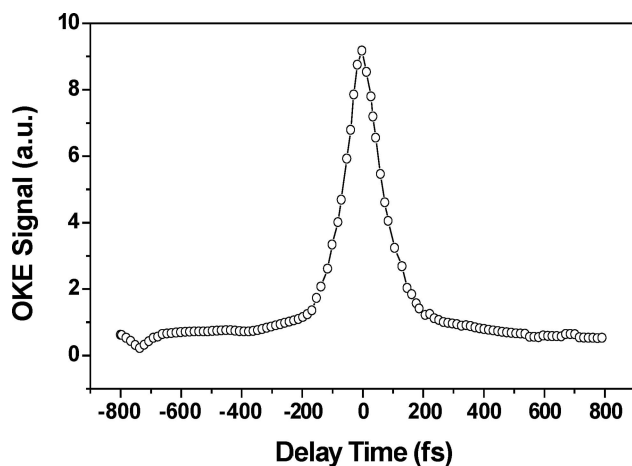


Figure 6 The ultrafast OKE response signals of PPIQCN10.

suggesting that the plasma polymerization has occurred mainly in the gas phase. In other words, the particles are formed in the gas phase and then deposited on the substrate [23]. The formation of spherical particles of about 9.5 nm in diameter in PPIQCN30 film supports the gas phase deposition mechanism at high discharge power.

The temporal evolution of OKE response of PPIQCN10 film is shown in Fig. 6. Since the absorption of PPIQCN10 film being negligible at the wavelength of 820 nm used in our laser, the non-resonant third-order nonlinearity of PPIQCN10 film could be measured using femtosecond optical Kerr technique at wavelength of 820 nm. From Fig. 6 it can be seen that PPIQCN10 film has a strong OKE signal, the third-order nonlinear susceptibilities ( $\chi^{(3)}$ ) calculated according to the reference [24] is  $8.8 \times 10^{-12}$  esu. The large non-linearity of PPIQCN10 film was attributed to the two-dimensional  $\pi$ -electron conjugation character of the large quinoline side group and the nitrogen atoms in the conjugation system [4]. It has been reported that the ultrafast optical response is derived from the delocalized  $\pi$ -electrons of conjugated system [25, 26]. Thus, it is reasonable to conclude that the more extensive the conjugated system is, the more evident the third-order optical nonlinearity may be. Furthermore, the non-resonant third-order nonlinear susceptibilities of the plasma PPIQCN10 film is large in comparison with that of plasma-polymerized benzonitrile ( $3.0 \times 10^{-12}$  esu) [17] indicating that the electron cloud of the quinoline ring would contribute more to the main chain than the benzene ring. The increase of the electron density on the conjugated  $C\equiv N$  backbone or the induced change in energetics leads to the increase of the third-order nonlinear susceptibilities [4]. Fig. 6 also shows that the signal profile of the PPIQCN10 film was approximately symmetric with a peak centred at zero delay point, which indicates a primarily pulse-width-limited response. To get the relaxation time of Kerr medium, the experimental curves were fitted with an exponential function [27]. It was observed that the time constant of PPIQCN10 film is approximately 130 fs that is slightly longer than the pulse duration (120 fs). Such an instanta-

neous response ensured that the measured NLO response was mainly contributed from the delocalized electrons. The large off-resonant third-order NLO susceptibility, ultrafast response time as well as adequate transparency of the plasma PPIQCN10 films may be applicable in the field of optical computing, optical signal processing and ultrafast nonlinear photonics [25]. For instance, the optical switch requires materials that combine suitably large optical nonlinearity with adequate transparency and fast response speed [28].

### 3. Conclusion

Studies on FTIR, UV-Vis, XPS, AFM, and OKE revealed that the plasma synthesis conditions affected the chemical structure, surface composition, morphology and property of the PPIQCN films. A transparent, smooth and homogeneous PPIQCN film with a large  $\pi$ -conjugated system can be formed at low plasma discharge power of 10 W; a high discharge power of 30 W can bring about more severe molecular (aromatic ring) fragmentation, and thus, the conjugation length of PPIQCN film decreases due to forming a non-conjugated polymer. The third-order nonlinear susceptibility ( $\chi^{(3)}$ ) of PPIQCN10 film in the non-resonant region is as large as  $8.8 \times 10^{-12}$  esu, larger than that of plasma-polymerized benzonitrile films. This indicates that the delocalized electrons of the quinoline ring would contribute more to the main chain than the benzene ring. Moreover, the ultrafast response was observed in PPIQCN10 film and the time constant was found to be approximately 130 fs.

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