Synthesis and Photoelectrical Properties of Poly[2,6-(p-phenoxy)-4-phenylquinoline]

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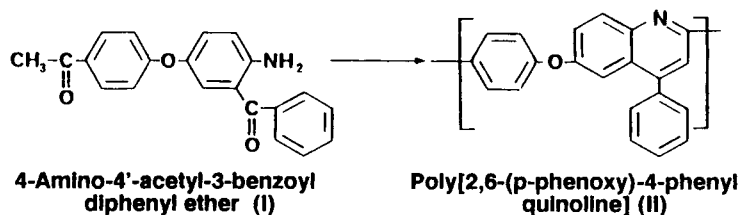
SYNOPSIS

New heteroaromatic polymer containing quinoline unit in the main chain, poly[2,6-(p-phenoxy)-4-phenyl quinoline] (PQ), was synthesized by the acid-catalyzed self-condensation reaction [Friedländer quinoline synthesis] of 4-amino-4'-acetyl-3-benzoyldiphenyl ether, and its chemical structure was characterized by IR and NMR spectra and also by elemental analysis. The PQ was soluble in common organic solvents such as chloroform or tetrahydrofuran; thus a strong coherent film of this polymer could be easily prepared from the solution by the casting or spin-coating technique. Attributing to the wholly aromatic chemical structure, PQ appeared an extremely high thermal stability as to show no weight loss up to 550°C both in air and nitrogen atmosphere. From the UV–VIS absorption spectra, we found that PQ had a strong tendency to form the charge transfer (CT) complex with electron acceptors such as 2,4,7-trinitrofluorenone (TNF). The CT complex film of PQ–TNF showed a good photoconductivity even under the ambient room illumination and was utilized for the fabrication of photovoltaic device whose conversion efficiency was around $10^{-2}\%$.

INTRODUCTION

Interests in the syntheses of aromatic polyquinolines have increased rapidly during the past decade because these materials display excellent oxidative and thermal stability.[1,2] Generally, high molecular weight polyquinolines can be prepared by an acid-catalyzed reaction of aromatic o-aminoketones with α-keto-methylene compounds, the Friedländer quinoline synthesis,[3–5] usually in good yields. Since the choice of monomer structure is versatile, wide variety of polyquinolines with different chain flexibility and thermal properties were prepared.[6–8] Among them, the rigid-rod polyquinolines have been widely investigated for fibers or films with excellent thermal stability and good mechanical properties. Although rigid-rod polyquinolines are characterized by their excellent thermal stability, high phase transition temperature, and high degree of crystallinity, their limited solubility in the conventional organic solvents has been the major obstacle for their practical applications.[9–10] Therefore, some compromise between the thermal properties and the processibility of polyquinolines should be made by the careful control of the monomer structure. From this viewpoint, we tried to synthesize a new semirigid polyquinoline containing flexible ether linkage in the main chain, poly[2,6-(p-phenoxy)-4-phenylquinoline], by the self-condensation of (4-amino-4'-acetyl-3-benzoyl) diphenyl ether.

4-Amino-4'-acetyl-3-benzoyl diphenyl ether (I)

Poly[2,6-(p-phenoxy)-4-phenyl quinoline] (II)

Recently, it was reported that several derivatives of polyquinolines can be doped with alkali metal donors[11,12] to show electrical conductivity as high

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as 10 S/cm under vacuum or inert gas atmosphere. All of the reports have been described for the doping of polyquinoline as electron acceptor with electron donors such as sodium naphthalide or sodium anthracide. Also they reported that the doped polyquinolines had been rapidly decreased in conductivity upon exposure to air.[11] There was no report for polyquinoline as electron donor and showing photoconductivity.

We have discovered that polyquinolines, which are normally excellent insulators, exhibit fairly good photoconductivity when doped with electron acceptors. The doped polyquinoline film was stable and its photoconductivity was not varied upon standing in air. Besides, polyquinoline films show the photovoltaic effect when treated with a solution of 2,4,7-trinitrofluorenone (TNF).

The subjects focused in this study are to combine the excellent oxidative and thermal properties of polyquinolines (PQ) and the electronic properties of quinoline rings. PQ is observed to have excellent thermal stability and is capable to form a stable film on solvent casting in common organic solvents. Then, we prepared uniformly doped films by mixing PQ as an electron donor with TNF as an electron acceptor and examined their photoconducting property. We also prepared a naked PQ film and treated it with a small amount of TNF solution.

EXPERIMENTALS

Syntheses of Monomers

4-Nitro-4'-(2-methyl-1,3-dioxolan-2-yl)diphenyl ether (III)

In a 1-L round-bottomed flask, equipped with Dean-Stark trap, a rapidly stirred solution of 52 g (0.2 mol) 4-nitro-4'-acetyldiphenylether, 45 mL of ethylene glycol, and 0.45 g p-toluene sulfonic acid in 200 mL toluene were placed and heated under reflux for 48 h. The yellowish brown solution was diluted with 500 mL toluene and washed three times with 50 mL 10% aqueous sodium hydroxide solution and then sufficiently with water. The toluene solution was concentrated to one-third of its original volume and allowed to cool. The yellow crystals obtained were collected by filtration: yield 86%; mp 83°C.

5-[p-(2-Methyl-1,3-dioxolan-2-yl)phenyl]-3-phenoxy-2,1-benzisoxazole (IV)

To a solution of 50 g of sodium hydroxide in 200 mL methanol at room temperature, 30 g benzylcyanide and 52 g of (III) were added. After 24 h vigorous stirring at 55°C, the light yellow amorphous solid precipitated, which was washed thoroughly with water and small portions of cold methanol to obtain light yellow needles: yield 84%; mp 118–118.5°C.

4-Amino-3-benzoyl-4'-(2-methyl-1,3-dioxolan-2-yl)diphenylether (V)

To a solution of 60.5 g of (IV) in 500 mL THF and 10 mL triethylamine, 6 g of 5% palladium on activated carbon was added. The vigorously stirred suspension was flushed with hydrogen and stirred at room temperature until the equivalent amount of hydrogen was absorbed. The catalyst was removed by filtration through a bed of Celite 545, and the solvent was removed under reduced pressure to afford yellow crystals.

4-Amino-4'-acetyl-3-benzoyldiphenyl ether (I)

To a solution of 35 g of (V) in 350 mL THF, 130 mL 0.6M HCl solution was added. The mixture was stirred at room temperature for 6 h and was added to 130 mL of water. After evaporating the THF under reduced pressure, a yellow precipitate was formed in the aqueous layer. The precipitate was collected by filtration and washed with water several times. The precipitate was then dissolved in chloroform, and the solution was washed with 10% aqueous sodium bicarbonate solution followed by water. After double recrystallization from methanol, bright yellow crystals of (I) were obtained: yield 82%; mp 121.5°C.

Anal: Calcd: C, 76.12%; H, 5.17%; N, 4.23%.
Found: C, 76.00%; H, 5.08%; N, 4.27%.

2,4-Diphenylquinoline (VI)

To a solution of 19.7 g (0.1 mol) of o-aminobenzophenone and 12 g (0.1 mol) of acetophenone in 200 mL glacial acetic acid, 10 mL concentrated sulfuric acid was added, and the solution was refluxed for 24 h. The reaction mixture was then cooled and dripped slowly into 550 mL of ice-cooled 4M ammonium hydroxide solution while stirring. The bright yellow crystals were obtained by extracting the yellow oily product with dichloromethane, followed by removing the solvent. The crystals were washed with hot water and recrystallized from ethanol to afford 23 g (yield 82%) of pale yellow crystals: mp 120.5–121°C.

Polymerization

Polymerization Medium

In a completely dried reactor, 200 mL of freshly distilled m-cresol and 85 g of phosphorus pentoxide were placed. The mixture was heated to 135–140°C

for 2.5–3.5 h with continuous stirring under a static nitrogen atmosphere. The resultant slightly yellow viscous liquid was a mixture of mono- and di-*m*-cresyl phosphate. The medium was freshly prepared just before each polymerization.

Polymerization

To a resin flask 5 mmol of (I) and the medium made of 8.5 g phosphorus pentoxide–20 mL *m*-cresol were added. The resin flask was purged with nitrogen, and the solution was stirred under a static nitrogen atmosphere at 140°C. The deep red polymerization solution was slowly poured into a 5–10% solution of triethylamine in ethanol. The resultant polymer precipitate was continuously extracted with ethanol for 24 h and dried at 90°C under reduced pressure.

Sample Preparation

PQ–TNF Mixture Film

The 5% solution of PQ-TNF in chloroform was poured onto a 2.5 × 2.5 cm² ITO glass. It was settled on a balanced base and covered with a petri dish to

reduce solvent evaporating. After being dried completely, a semitransparent gold electrode of 1.5 cm² was deposited by high-vacuum evaporation on the PQ-TNF mixture film, and each electrode was connected with tin foil using small amount of silver paste.

TNF-Treated PQ Film

The semitransparent gold electrode was made by vacuum evaporation onto a 2.5 × 2.5 cm² slide glass. PQ film was cast on this electrode using a spin coater. After drying the solvent completely, a 2–3% solution of TNF in methylethylketone was dropped onto the PQ film and then spread using spin coater. Then, Al as a counter electrode was evaporated on the completely dried film with 1.5 cm² area.

Characterization

Spectrometries

All the IR spectra were obtained on a Alpha Centauri Fourier transform infrared spectrometer of Mattson
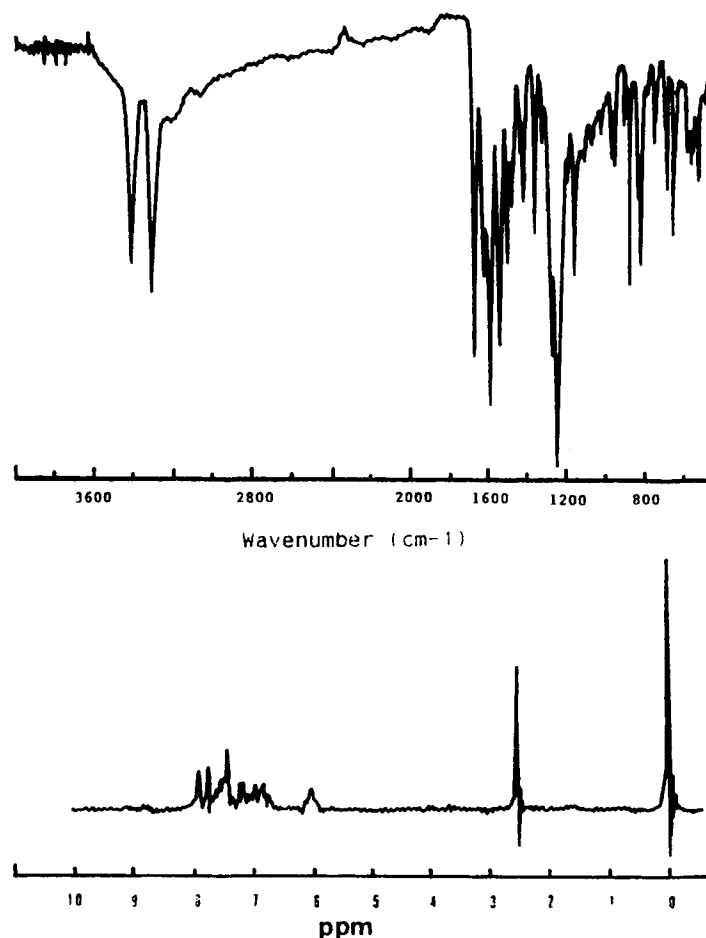

Figure 1   IR and NMR spectra of 4-nitro-4'-acetyldiphenylether.

Instruments, Inc. at a resolution of 4 cm^{-1} at room temperature. NMR Spectra were obtained at room temperature on a Jeol JLM-PMX 60 SI NMR spectrometer with tetramethylsilane as an internal standard.

Elemental Analysis

A Perkin-Elmer elemental analyzer model 240DS was used for the elemental analyses of the monomer.

Thermogravimetric analysis (TGA)

A Rigaku 8150 thermogravimetric system was used. The sample was heated at a rate of 10°C/min under dry nitrogen and air.

Photoconductivity Measurements

The dark- and photoconductivity of PQ–TNF mixture film were measured using a Keithley Model 617 electrometer. The photoconductivity was measured in room illumination (0.06 mW/cm^2) using a fluorescent lamp.

Photovoltaic Property

The TNF-treated PQ film between Au and Al electrodes was connected to the electrometer for measuring the photovoltaic property: Au(+) biased. The voltage range was from −3 to 3 V, and light source was USHIO mercury lamp Model UI-501C.

RESULTS AND DISCUSSION

Figure 1 shows the IR and NMR spectra of 4-nitro-4'-acetyldiphenyl ether. In the IR spectra, a characteristic doublet absorption band of an aromatic primary amine (3500–3300 cm^{-1}), carbonyl stretchings of acetyl (1670 cm^{-1}), and benzophenone (1625 cm^{-1}) units, a strong single peak of an ether linkage (1230 cm^{-1}), and signals of mono, para-di,
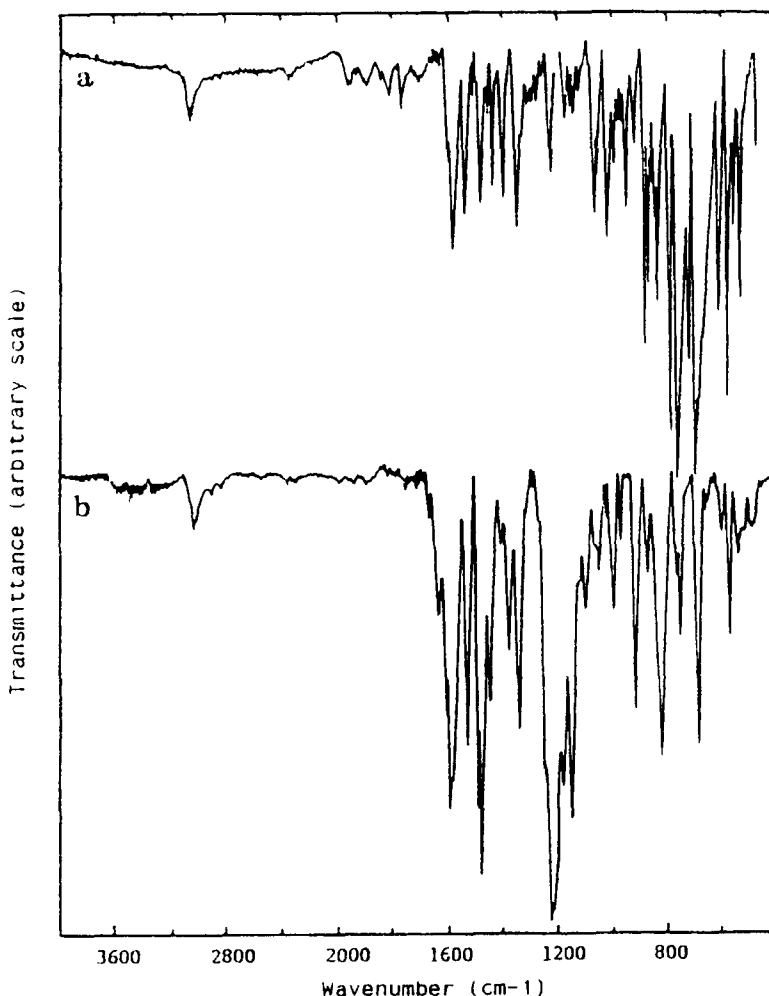

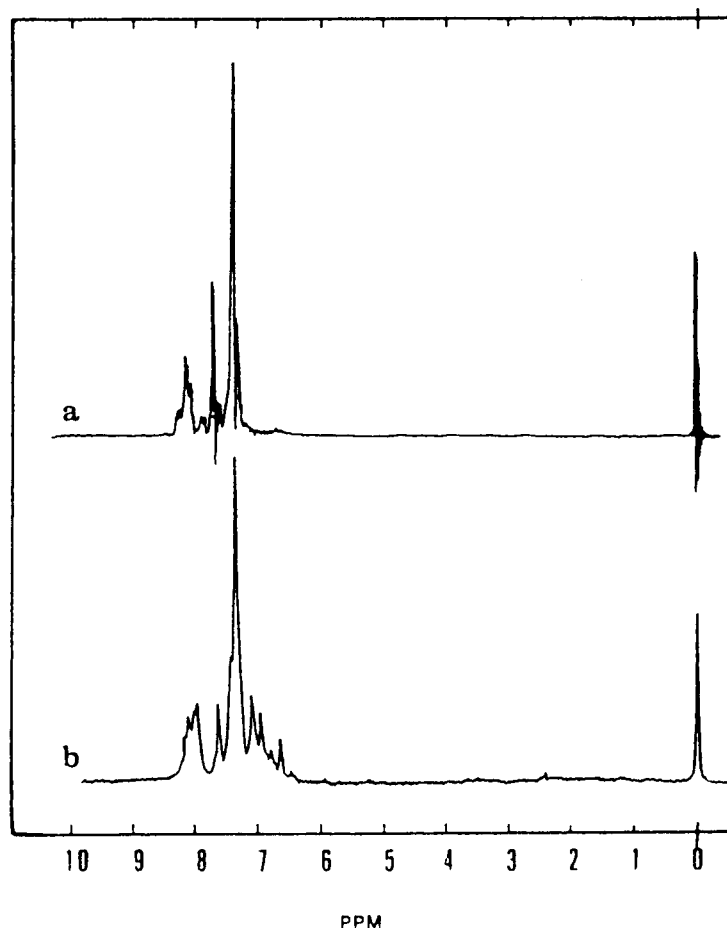**Figure 2**   IR spectra of (a) 2,4-diphenylquinoline and (b) PQ.

Figure 3   NMR spectra of (a) 2,4-diphenylquinoline and (b) PQ.

and 1,2,4-tri-substituted benzenes at 880–690 cm^{-1} were found. The NMR spectra show the amine proton of o-aminoketone at 6.9–7.2 ppm and the methyl proton of an aromatic acetyl group appear at 2.5 ppm.

The IR and NMR spectra of PQ were compared with those of 2,4-diphenylquinoline (Figs. 2 and 3). The comparison showed that the polymer have the quinoline structure. The peaks seen at 1270–1240 and 1165 cm^{-1} for PQ indicate the existence of ether linkage, and the peak at 830 cm^{-1} is due to p-phenylene. Proton NMR spectra shows that the PQ has the similar structure to 2,4-diphenylquinoline.

The crystalline transition temperature of PQ was not detected; however, a glass transition was found at 235.4°C. The stability against thermal decomposition of PQ was studied by TGA by the dynamic temperature method. Thermogravimetric traces of the PQ in air and inert atmosphere are shown in Figure 4. The extrapolated onsets of decomposition for PQ are 551.7°C (in nitrogen) and 548.5°C (in air).

When PQ was doped with TNF as an electron acceptor, the color was immediately changed from light yellow of the original PQ to dark orange, which
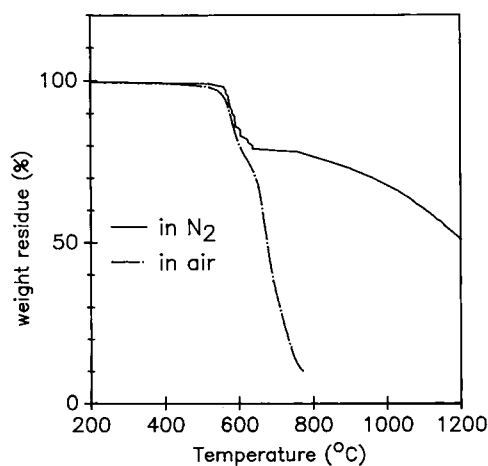

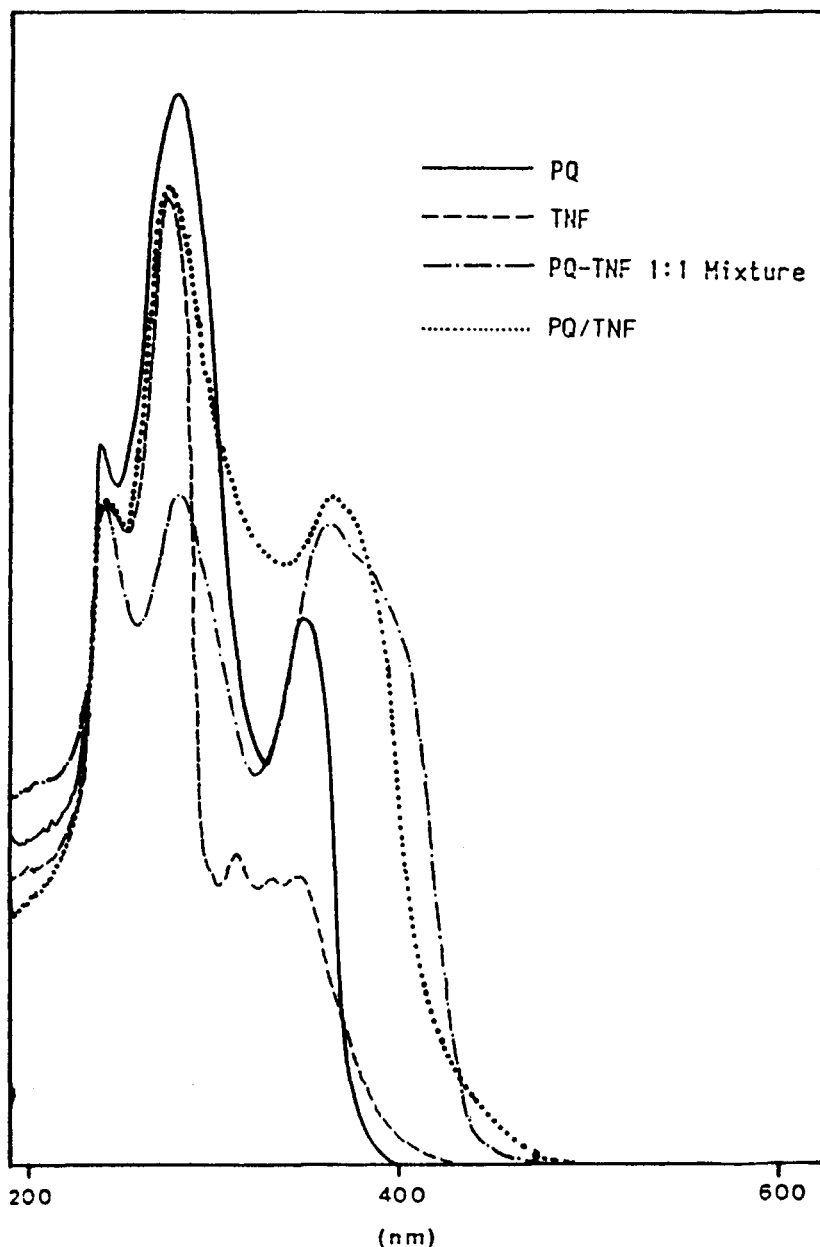**Figure 4**   TGA thermogram of PQ with heating rate of 10°C/min.

Figure 5 UV spectra of PQ and PQ–TNF mixture.

indicates the formation of charge transfer (CT) complexes, as shown in Figure 5, the UV–visible spectra of PQ, TNF, PQ–TNF 1 : 1 mixture, and TNF-treated PQ thin film. In the spectrum of the sample, which had been made by layering the TNF on PQ layer, the similar trend was observed.

The dark and photo current density versus electric field characteristics for PQ doped with TNF are shown in Figure 6. The photo current was 1.7×10^{-7} A/cm^2 at 1×10^5 V/cm, and the dark current was 1.1×10^{-8} A/cm^2 at the same electric field. The difference was increased with the increase of the electric field. At low electric field, the log current

was proportional to log field, but when the field was increased, the rate was increased.

Figure 7 shows the I–V characteristics for PQ thin film of which the surface was treated with TNF solution to form the CT complex at the interface. The photocurrent were 10^2–10^3 times larger than the dark current. Illuminated at the wavelength regions between 390 and 510 nm, the photovoltaic current was observed at 0–0.67 V in the system as shown in the other many organic polymers of p-type semiconductor when they were contacted to the Al electrode. Such photovoltaic currents may be due to a potential barrier, the Schottky barrier, at the inter-
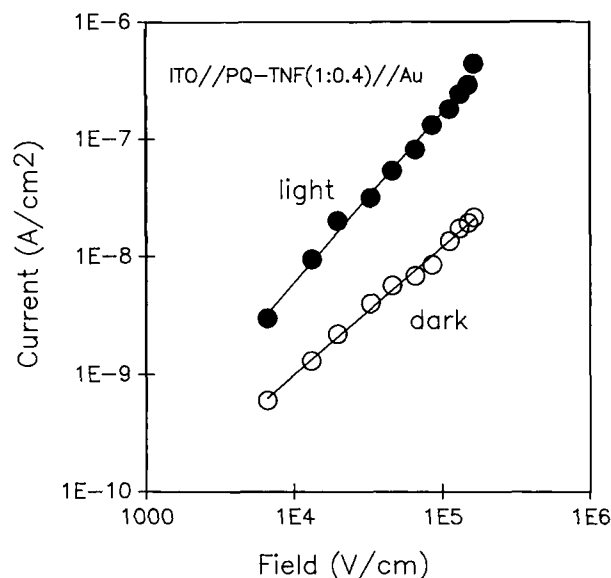
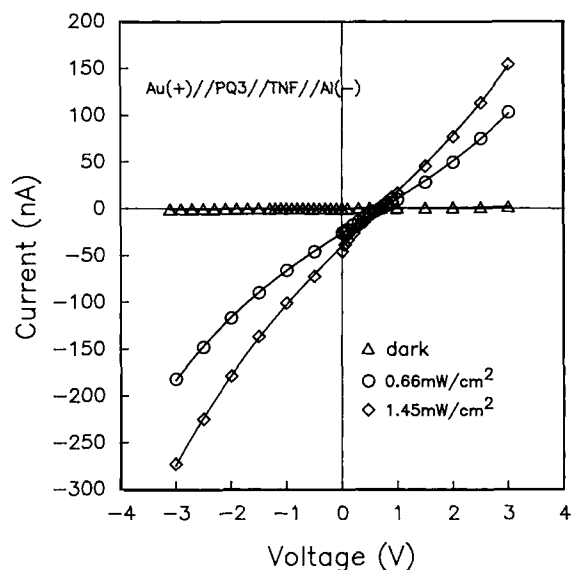**Figure 6**   Field dependence of photo and dark current in PQ–TNF 1 : 0.4 mixture.

Figure 7   I–V curves of PQ–TNF double-layered cell at various irradiation.

face between metal electrodes and an n-type layer of PQ–TNF complex and to a difference in the work functions in the electrodes for Au and Al. The photovoltaic current at 0 V (I_{sc}, short circuit current)

was increased with increasing radiation, and the open circuit voltage, V_{oc}, is not varied largely at around 0.65–0.7 V. The photovoltaic conversion efficiency, η, was calculated to be 4.5×10^{-3}–$3 \times 10^{-2}\%$.

CONCLUSIONS

The semirigid polyquinoline, poly[2,6-(p-phenoxy)-4-phenylquinoline](PQ) was prepared by an acid-catalyzed reaction of aromatic o-aminoketone with α-ketomethylene compounds. PQ has the excellent thermal and mechanical properties and also has the processibility. PQ could form the CT complex with TNF, and the complex showed photoconductivity and photovoltaic properties.

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