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

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ABSTRACT: New heteroaromatic polymer containing quinoline moiety in the main chain, poly[2,6-(p-phenylsulfanyl)-4-phenylquinoline] (PQ-S) was synthesized by the Friedländer reaction of 1-[4-(4-aminoo-3-benzoylphenylsulfanyl)phenyl]ethanone and identified by IR, NMR, and elemental analysis. Due to the wholly aromatic chemical structure, PQ-S showed a high glass transition temperature of 235 °C, and also excellent thermal stability revealed by initial decomposition temperature (onset temperature) as high as 513 °C. PQ-S was soluble in several organic solvents such as chloroform and tetrachloroethane so that transparent thin film could be easily prepared from the solution by spin coating method. From the UV-visible absorption and emission spectra, the characteristic photoluminescence of PQ-S centered at around 420 nm was observed. It was also found that PQ-S could form the charge transfer complex with 2,4,7-trinitrofluorenone (TNF), a well-known electron acceptor.

Keywords: polyquinoline, thermal stability, charge transfer complex, photoluminescence.
INTRODUCTION

Polyquinolines were developed during the 1970’s in response to increasing demand for polymeric materials with high thermal and oxidative stability.\(^\text{12}\) Generally, polyquinolines are prepared by the acid-catalyzed reaction of \(\sigma\)-amino aromatic aldehyde or ketone with \(\alpha\)-ketomethylene compound, in good yields. Recently, it was reported that some wholly aromatic polyquinolines, which are normally excellent electrical insulators, showed electrical conductivity as high as 10 S/cm under vacuum or inert gas atmosphere when doped either with electron donors or by electrochemical reduction.\(^\text{3-5}\) It is well known that thermally stable polymers containing rigid totally aromatic or heteroaromatic backbone, generally exhibit high glass transition temperatures and poor solubility. To enhance the solubilities of rigid rod polyquinolines, thermally stable flexible linkages such as ether, sulfide, sulfone, and carbonyl groups are introduced to the main chain, and these flexible linkages lower the glass transition temperature and increase the solubility. High molecular weight semirigid polyquinolines can be obtained from the bis (aminoketone) monomers (A-A type) containing an oxygen link between the aromatic units and bis (ketomethylene) monomers (B-B type). Semirigid polyquinolines from the monomer containing both the ketomethylene moiety and the aminoketone group in one molecule (A-B type) are rare. Among them, poly[2, 6-(\(p\)-phenoxy)-4-phenylquinoline] (PQ-O), in our earlier work, showed extremely high thermal stability and good solubility in common organic solvents such as chloroform or tetrahydrofuran. PQ-O was found to form the CT complex with 2, 4,7-trinitrofluorenone (TNF) or 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) and both the mixtures showed photoconductivity and photovoltaic properties.\(^\text{6}\) In this work, we synthesized a novel polyquinoline with sulfide linkage from a A-B type monomer, as an extension of our polyquinoline study.\(^\text{7}\) PQ-S is expected to show good photoconductive properties as a result of the richer electron density of sulfur atom than that of oxygen, while maintaining the excellent thermal and mechanical properties and processibility.

EXPERIMENTAL

Materials. Nitrothiophenol and 4’-aminoaceto- phenone (Tokyo Kasei Kogyo Co., Ltd.) were used without further purification. \(p\)-Toluenesulfonic acid was recrystallized from ethanol/water. Palladium on activated carbon (5%, Fluka) was used as received.

Monomer Synthesis.

1-[4-(4-nitrophenylsulfanyl)phenyl]ethanone (I): 3.88 g (0.02 mol) of nitrothiophenol was dissolved in a solution of 4.4 g of sodium hydroxide and 100 mL of water, and then heated to 72°C. 2.7 g (0.02 mol) of aminoacetophenone was dissolved in 6.25 g of concentrated hydrochloric acid (35%) and 30 mL of water and then diazotized in the usual manner with an aqueous solution of 2.04 g of sodium nitrite. The cold solution of diazotized aminoacetophenone was slowly dropped with constant stirring into the alkaline thiophenate solution which was held at 72°C. A yellow precipitate was formed which rapidly decomposed with the evolution of nitrogen gas. The reaction mixture was heated to 74°C, and then stirred overnight. The resultant brown reaction mixture was filtered, washed with water. Recrystallization from methanol afforded 2.60 g (47.5%) of I: mp 119-120°C; IR (KBr) 1680 (CH\(_3\)C=O), 1510 and 1335 (NO\(_2\)), 1085 (Ar-S-Ar) cm\(^{-1}\); \(^1\)H NMR (CDCl\(_3\)) \(\delta\) 8.06 (d, 2H), 7.89 (d, 2H), 7.46 (d, 2H), 7.29 (d, 2H), 2.55 (s, 3H). Anal. Calcd for C\(_{14}\)H\(_9\)NO\(_2\)S: C, 61.53; H, 4.06; N, 5.12; S, 11.73. Found: C, 61.48; H, 3.81; N,
5.15; S, 11.83.

2-methyl-2-[4-(4-nitrophenoxy)sulfanyl]phenyl]-[1,3]-dioxolane (2): A rapidly stirred solution of 2.60 g (9.5 mmol) of 1, 1.68 mL (0.03 mol) of ethylene glycol, and 0.1 g (0.5 mmol) of p-toluenesulfonic acid in 50 mL toluene was heated to reflux for 48 h in a 100 mL flask equipped with a Dean-Stark trap. The reaction mixture was washed twice with 50 mL of 10% aqueous sodium hydroxide solution and then washed with water until neutral. After the organic layer was decolorized with charcoal, the solvent was evaporated, and recrystallized from methanol. A total of 2.65 g (94.7%) of yellow crystal was obtained: mp 112-114 °C; IR (KBr) 1514 and 1338 (NO₂), absence of 1680 (CH₂C=O) cm⁻¹; 1H NMR (CDCl₃) δ 8.05 (d, 2H), 7.5 (m, 4H), 7.17 (d, 2H), 3.8-4.09 (m, 4H), 1.67 (s, 3H). Anal. Calcd for C₁₉H₁₈NO₅S: C, 60.55; H, 4.76; N, 4.41; S, 10.10. Found: C, 61.5; H, 4.0; N, 5.06; S, 11.7.

5-[4-(2-methyl-[1,3]-dioxolan-2-yl)-phenylsulfanyl]-3-phenyl-benz[e]isoxazole (3): 8 g (0.2 mol) of sodium hydroxide was added to 50 mL of methanol and the solution was allowed to cool down to room temperature. To this solution, 9.64 mL (0.080 mol) of benzylcyanide and 11.67 g (0.040 mol) of 2 in 25 mL of tetrahydrofuran were added. The reaction mixture was stirred at room temperature for 1 h, and then at 65 °C for 24 h. After the resulting brown solution was cooled in an ice bath, the solution was poured into excess water. Dark brown precipitate was isolated by suction filtration, washed with water and cold methanol. Recrystallization from methanol yielded 8.71 g (56%) of 3: mp 123-124 °C; IR (KBr) 1626 (C=O), abscence of 1514 and 1338 (NO₂) cm⁻¹; 1H NMR (CDCl₃) δ 7.2-8.0 (m, 12H), 3.78-4.02 (m, 4H), 1.65 (s, 3H). Anal. Calcd for C₂₃H₂₁NO₅S: C, 70.93; H, 4.92; N, 3.60; S, 8.23. Found: C, 70.68; H, 4.50; N, 3.79; S, 8.42.

[2-amino-5-[4-(2-methyl-[1,3]dioxolan-2-yl)phenoxy)sulfanyl]phenyl]-phenyl-methanone (4): To a solution of 8.71 g (22.36 mmol) of 3 in 80 mL of tetrahydrofuran and 2.62 mL of triethylamine was added 0.75 g of 5% palladium on activated carbon. The vigorously stirred suspension was degassed by handy aspirator in an ice bath, and then flushed with hydrogen and stirred at room temperature under ordinary pressure until the absorption of hydrogen ceased. The catalyst was removed by filtration through a bed of Celite 545 and the solvent was removed under reduced pressure. Recrystallization from 5:1 methanol/tetrahydrofuran afforded 6.46 g (76%) of 4: mp 115-116 °C; IR (KBr) 3450 and 3350 (NH₂), 1620 (PhC=O) cm⁻¹; 1H NMR (CDCl₃) 6.8-7.7 (m, 12H), 6.30 (s, 2H), 3.74-4.02 (m, 4H), 1.62 (s, 3H). Anal. Calcd for C₂₅H₂₃NO₅S: C, 70.57; H, 5.41; N, 3.58; S, 8.19. Found: C, 70.7; H, 5.45; N, 3.55; S, 8.19.

1-[4-(4-amino-3-benzoylphenylsulfanyl)phenyl]ethanone (5): A solution of 6.99 g (17.9 mmol) of 4 in 27 mL of hydrochloric acid was stirred at room temperature for 6 h and then 30 mL of water was added. The tetrahydrofuran was removed under reduced pressure, when a yellow precipitate was formed in the water layer. The yellow precipitate was collected by suction filtration and then washed with water thoroughly. The precipitate was then dissolved in chloroform and washed with 10% aqueous sodium bicarbonate solution followed by water. The chloroform was removed, and recrystallization from methanol afforded 3.49 g (55.9%) of 5: mp 118-120 °C; IR (KBr) 3460 and 3350 (NH₂), 1675 (CH₃C=O), 1618 (PhC=O),1085 (Ar-S-Ar) cm⁻¹; 1H NMR (CDCl₃) δ 6.8-7.8 (m, 12H), 6.4 (s, 2H), 2.59 (s, 3H). Anal. Calcd for C₂₁H₁₇NO₅S: C, 72.06; H, 4.94; N, 4.03; S, 9.21. Found: C, 72.7; H, 4.94; N, 4.02; S, 9.21.

Polymerization. In a completely dried reactor,
20 mL of freshly distilled \( m \)-cresol and 8.5 g of phosphorus pentoxide were placed. The mixture was heated to 140 °C for 2.5-3.5 h with continuous stirring under nitrogen gas flow. The resultant viscous liquid was a mixture of mono- and di-\( m \)-cresyl phosphate. This reaction medium was freshly prepared just before each polymerization. The polymerization medium was cooled to room temperature, followed by the addition of 5 mmol (1.7372 g) of 5. The reaction mixture was stirred under nitrogen atmosphere at 140 °C for 48 h. The deep red polymerization solution was slowly poured into a 10:1 (v/v) mixture of ethanol and triethylamine. The resultant polymer precipitate was washed with ethanol, and then continuously extracted with hot ethanol for 24 h and air dried. The dried polymer precipitate was redisolved in chloroform and slowly poured into excess of ethanol, the precipitate was filtered, and dried under reduced pressure. After drying, 1.06 g (61%) of PQ-S was obtained. The inherent viscosity of the polymer was 0.59 dL/g in chloroform at 25 °C. Anal. Calc'd for (C\(_{21}\)H\(_{13}\)NS)\(_n\): C, 81.00; H, 4.21; N, 4.50; S, 10.30. Found: C, 80.08; H, 4.08; N, 4.57; S, 10.51.

**Measurements.** Infrared spectra were recorded from neat film or potassium bromide (KBr) pellets on a Micad FT-IR spectrophotometer. A Bruker AMX 500 (500MHz) and a Varian 200 (200MHz) were used for NMR measurements. Elementar analyses were carried out with a Carlo Erba 116 Elemental Analyzer. Inherent viscosity of PQ-S was determined at a concentration of 0.5 g/dL with Ubbelode viscometer. Differential scanning calorimetry (DSC) analyses were performed on a Perkin Elmer DSC7 at a heating rate of 10 °C/min, and thermogravimetric analyses (TGA) were conducted with a Du Pont 2950 at a heating rate of 10 °C/min under nitrogen atmosphere. UV-visible spectra were recorded on a Shimadzu UV-2101PC double beam spectrophotometer and a HP 8452A diode array spectrophotometer. Photoluminescence (PL) spectra were obtained using ISS K2 multifrequency phase fluorometer equipped with 300W xenon arc lamp.

**RESULTS AND DISCUSSION**

Synthetic routes of monomer 5 and PQ-S are shown in Scheme 1. The Ziegler reaction\(^6\) was used to introduce sulfide linkage between nitrothiophenol and 4'-aminoacetophenone, fol-
Figure 1. IR and $^1$H-NMR spectra of 1-[4-(4-amino-3-benzoylphenylsulfanyl)phenyl]ethanone.

Figure 2. IR and $^1$H-NMR spectra of PQ-S.

Figure 3. DSC thermogram of PQ-S at a heating rate of 10 °C/min.

8.2 ppm appeared except solvent peak. And PQ-S was soluble in several organic solvents such as chloroform and tetrachloroethane.
The melting temperature of PQ-S was not detected, however a glass transition temperature was found at 235 °C (Fig. 3) by DSC. The thermal stability of PQ-S was studied by thermogravimetric analysis. Thermogravimetric trace of PQ-S in nitrogen atmosphere is shown in Fig. 4. The 10% decomposition temperature of PQ-S was 545 °C, and the extrapolated onset of decomposition was 513 °C.

When PQ-S was doped with 2,4,7-trinitrofluorenone (TNF) as an electron acceptor, the color changed immediately from light yellow of the pristine PQ-S to dark red, which indicates the formation of charge transfer (CT) complex, as shown in Fig. 5. The observed CT band, due to the CT complex formation between the HOMO of PQ-S and LUMO of the TNF, strongly suggests the potential photoconductivity of PQ-S/TNF much like that of PQ-O/TNF reported earlier. Fig. 6 shows the UV absorption and photoluminescence spectra of PQ-S. The UV-visible maximum absorption peak was 374 nm, and the photoluminescence maximum wavelength excited at 375 nm was around 415-430 nm.

CONCLUSIONS

The semirigid polyquinoline, poly[2,6-(p-phenyl-sulfanyl)-4-phenylquinoline] (PQ-S) was prepared by the Friedländer quinoline synthesis. PQ-
S showed excellent thermal properties together with good solubility. PQ-S could form CT complex with TNF, and showed photoluminescence maximum wavelength at around 415-430 nm. The studies on photoductivity and photovoltaic effect of CT complex of PQ-S with TNF are in progress.

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REFERENCES