

Poly[2,6-(*p*-phenylsulfanyl)-4-phenylquinoline]의 합성과 특성

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

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요 약: 주쇄에 퀴놀린 단위를 함유하는 새로운 복소환 고분자인 poly[2,6-(*p*-phenylsulfanyl)-4-phenylquinoline] (PQ-S)를 1-[4-(4-amino-3-benzoylphenylsulfanyl)phenyl]ethanone의 Friedländer 반응에 의해 합성하였으며, IR, NMR, 원소분석을 통해 구조를 확인하였다. PQ-S는 전방향족 화학구조로 인해 235 °C의 높은 유리전이온도와 초기분해온도가 513 °C인 높은 열안정성을 보였다. PQ-S는 클로로포름이나 테트라클로로에탄과 같은 유기용매에 뛰어난 용해성을 보여 스핀 코팅법에 의해 균일한 박막을 손쉽게 제조할 수 있었다. UV-visible 흡수 및 방출스펙트럼을 통해 PQ-S는 420 nm을 최대파장으로 하는 photoluminescence를 보임을 확인하였으며, 또한 대표적인 전자받게인 2,4,7-trinitrofluorenone과의 전하 이동 착체를 형성함을 알 수 있었다.

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-amino-3-benzoylphenylsulfanyl)phenyl]ethanone, and its chemical structure was 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.^{1,2} Generally, polyquinolines are prepared by the acid-catalyzed reaction of *o*-amino aromatic aldehyde or ketone with α -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.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.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.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'-aminoacetophenone (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 (1): 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 thiophenolate solution which was held at 72 °C. A yellow precipitate was formed which rapidly decomposed with the ebullition 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 **1**: mp 119-120 °C; IR (KBr) 1680 (CH₃C=O), 1510 and 1335 (NO₂), 1085 (Ar-S-Ar) cm⁻¹; ¹H NMR (CDCl₃) δ 8.06 (d, 2H), 7.89 (d, 2H), 7.46 (d, 2H), 7.29 (d, 2H), 2.55 (s, 3H). Anal. Calcd for C₁₄H₁₁NO₂S: 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-nitrophenylsulfanyl)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 (CH₃C=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 C₁₆H₁₉NO₃S: 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-benzo[c]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 benzylocyanide 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=N), absence 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 C₂₃H₁₉NO₃S: 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)

phenylsulfanyl]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 C₂₃H₂₁NO₃S: 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.

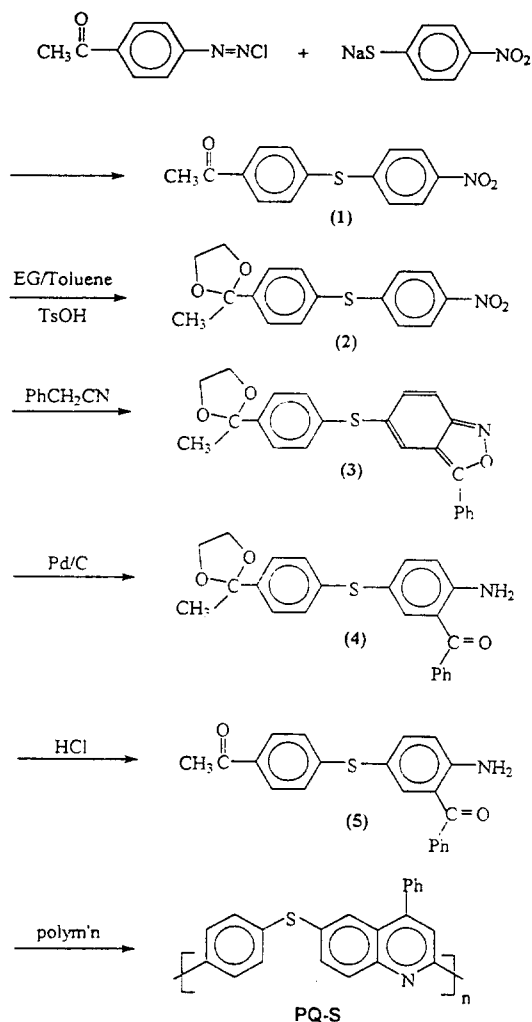
1-[4-(4-amino-3-benzoylphenylsulfanyl)

phenyl]ethanone (5): A solution of 6.99 g (17.9 mmol) of **4** in 67 mL of tetrahydrofuran and 27 mL of 0.6 N 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 C₂₁H₁₇NO₂S: 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 redissolved 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. Calcd 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 Midac FT-IR spectrophotometer. A Bruker AMX 500 (500MHz) and a Varian 200 (200MHz) were used for NMR measurements. Elemental 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



Scheme 1. Synthesis of PQ-S.

meter 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 reaction⁸ was used to introduce sulfide linkage between nitrothiophenol and 4'-aminoacetophenone, fol-

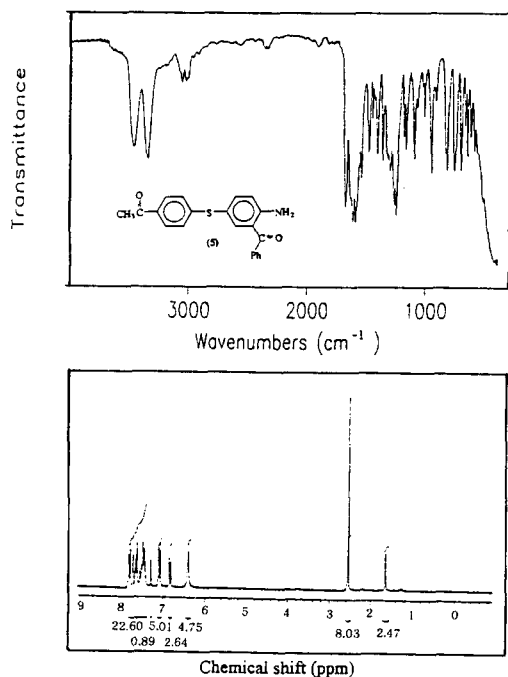


Figure 1. IR and ¹H-NMR spectra of 1-[4-(4-amino-3-benzoylphenylsulfanyl)phenyl]ethanone.

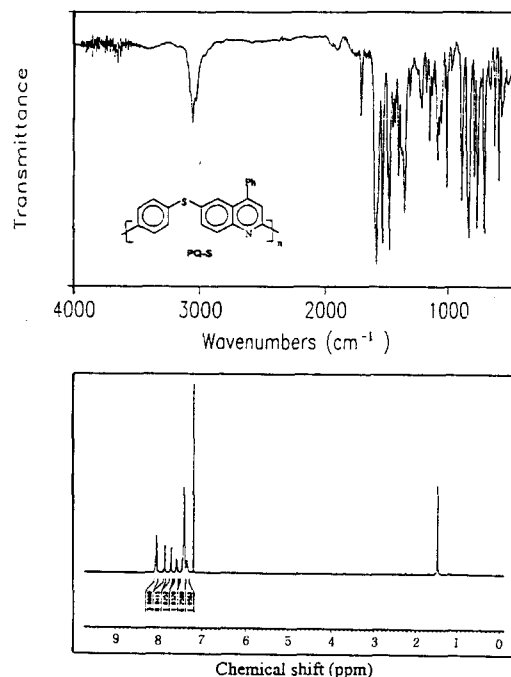


Figure 2. IR and ¹H-NMR spectra of PQ-S.

lowed by a sequence of reactions leading to the high molecular weight PQ-S. Fig. 1 and 2 show the IR and ¹H-NMR spectra of 1-[4-(4-amino-3-benzoylphenylsulfanyl)phenyl]ethanone (5) and PQ-S. In the IR spectrum of 5, a characteristic doublet absorption band of an amine (3350, 3460 cm⁻¹), carbonyl stretchings of acetyl (1675 cm⁻¹) and benzophenone (1618 cm⁻¹) units and a single peak of an aromatic sulfide (1085 cm⁻¹) appeared. And the twelve aromatic protons at 6.8–7.8 ppm, primary amine protons at 6.4 ppm, and methyl protons of an aromatic acetyl group at 2.59 ppm in the ¹H-NMR spectrum of Fig. 1 confirmed the structure of 5. In the IR spectrum of PQ-S, a characteristic doublet absorption band of an amine, carbonyl stretchings of acetyl and benzophenone units disappeared except a single peak of an aromatic sulfide. As shown in ¹H-NMR spectrum of PQ-S, only aromatic protons at 7.1–

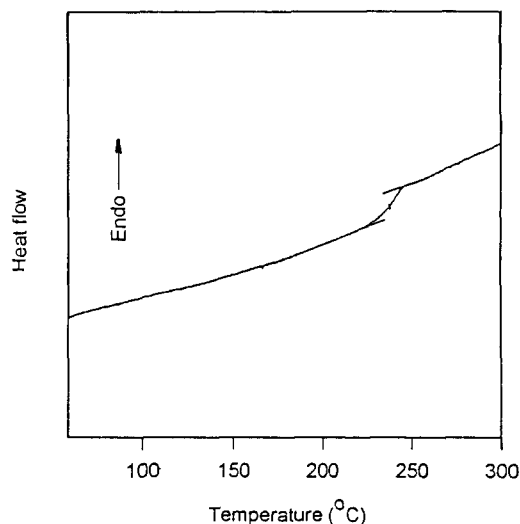


Figure 3. DSC thermogram of PQ-S at a heating rate of 10 °C/min.

8.2 ppm appeared except solvent peak. And PQ-S was soluble in several organic solvents such as chloroform and tetrachloroethane.

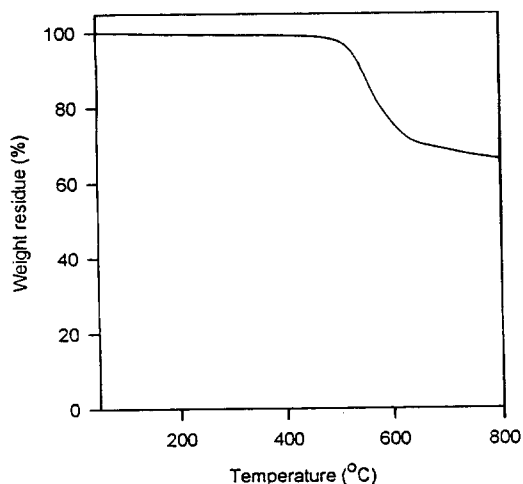


Figure 4. TG thermogram of PQ-S at a heating rate of 10 °C/min.

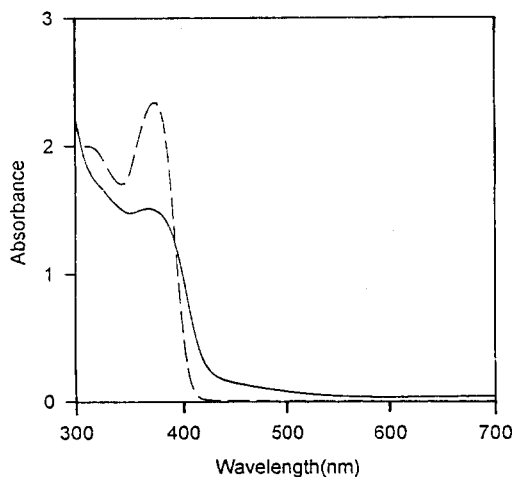


Figure 5. UV-visible spectra of PQ-S (dashed line) and PQ-S/TNF mixture (solid line).

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 decom-

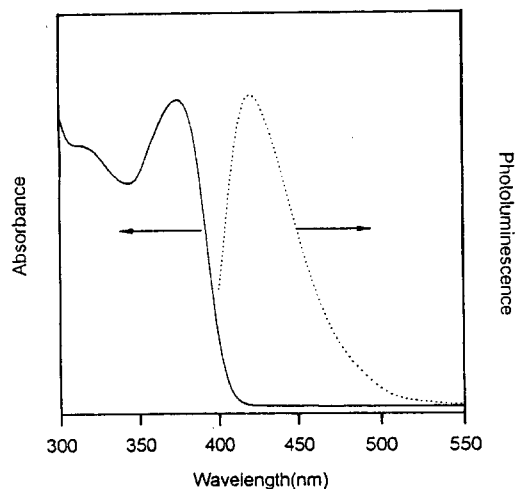


Figure 6. UV-visible (solid) and photoluminescence (dashed) spectra for PQ-S. Intensities of absorption and emission are arbitrarily scaled to the same ordinate scale to allow comparison of wavelength maxima and line shapes. All spectra were obtained in chloroform solution.

position 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.⁷ 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*-phenylsulfanyl)-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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