

Synthesis and Properties of Polyquinolines and Polyanthrazolines Containing Pyrrole Units in the Main Chain

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Introduction

Polyquinolines were developed during the 1970's by Stille and co-workers in response to increasing demand for polymeric materials with high thermal and oxidative stability.^{1,2} Recently, optical and electronic properties of polyquinolines such as electroluminescent,³ third order nonlinear optical,⁴ and optically active properties,⁵ have been studied extensively for their potential use in photonics and electronic applications.

In this report, a series of 8 new polyquinolines and polyanthrazolines with pyrrole isomeric units in main chain were synthesized and characterized. The new polymers are expected to have improved thermal and electronic properties for applications and serve as model systems for investigating structure-property relationships in conjugated polymers.

Experimental Section

Monomer Synthesis 4,4'-Bis(2-aminobenzoyl)diphenyl ether (A), 2,5-dibenzoyl-1,4-phenylene Diamine (C), 4,6-dibenzoyl-1,3-phenylenediamine (D) and 4,4'-diamino-3,3'-dibenzoyldiphenyl ether (B) were synthesized according to the literature.¹ 2,5-Diacetylpyrrole (o) and 2,4-diacetylpyrrole (m) were prepared according to the process in Scheme 2.

1-(p-tolylsulfonyl) pyrrole 1 To a vigorously stirred solution of 43.6 mL (0.60 mol) of pyrrole and 400 mL of absolute tetrahydrofuran at 25°C was slowly added 20 g (0.50 mol) of metal potassium. The mixture was allowed to heat to the reflux temperature and maintained at reflux until all of the metal had reacted (about 3 h). Heating was then discontinued. The white slurry was diluted with 350 mL of solvent, and a solution of 76.2 g (0.40 mol) of p-tolylsulfonyl chloride in 450 mL of tetrahydrofuran added dropwise over a period of 45 min. After the resulting mixture had been stirred at room temperature overnight, it was filtered to yield a solution which was evaporated to dryness under reduced pressure, the solid residue was treated with activated charcoal and recrystallized from methanol to give 53.9 g (61.0%) of white crystals, mp 105-106 °C.

1-(p-Tolylsulfonyl)-2-acetylpyrrole 2 To a solution of acetic anhydride (27 g, 0.26 mol) in 720 mL of 1,2-dichloroethane at 25°C was added BF₃·OEt₂ (75 g, 0.52 mol). The mixture was stirred for 10 min, 1-(p-Tolylsulfonyl) Pyrrole (50 g, 0.23 mol) in 240 mL of 1,2-dichloroethane was added, and the mixture was stirred at 25°C for 2 h. The reaction was quenched with cold water, and the residue remaining after concentration at reduced pressure was recrystallized from chloroform-hexane (1:5) to afford 48.9 g (80.5%) of pure 2, mp.110-111°C.

2-Acetylpyrrole 3 To a stirred solution of 45 g (0.17 mol) of 1-(p-Tolylsulfonyl)-2-acetylpyrrole in 300 mL of methanol was added dropwise 300 mL of 5 M NaOH at room temperature. The solution was heated and refluxed for 4 h. After the methanol was evaporated at reduced pressure, the aqueous residue was extracted with ethyl acetate, and the extracts were washed with brine, dried over Na₂SO₄, and concentrated at reduced pressure to give 17.5 g (94.4%) of 2-acetylpyrrole

3, mp.89-90°C.

2,5-Diacetylpyrrole (o) and 2,4-diacetylpyrrole (m) To a stirred mixture of 14.2 g (0.234 mol) of glacial acetic acid and 37.8 g (0.390 mol) of trifluoroacetic anhydride under N₂ was added dropwise a solution of 17 g (0.156 mol) of 2-acetylpyrrole in 235 mL of dry benzene. The whole was stirred for 2 weeks at room temperature during which the color turned from cranberry to black. The mixture was poured into 160 mL of water containing 80 g (0.94 mol) of sodium bicarbonate, and the resulting solution (pH is about 7) was extracted with ethyl acetate (6×150 mL). The aqueous layer was set aside. Evaporation of the solvent from the dried (magnesium sulfate) extract left 24 g of black solid which was triturated with 3×40 mL of hot water for 2 h. The cooled filtrate was added 45 g of sodium chlorate and extracted with ethyl acetate (6×150 mL). Removal of the solvent from the dried extract gave 15.1 g of solid which was chromatographed in a column of silica gum (100-200 mesh). Elution with 2:1 petroleum ether-diethyl ether afforded three products. The first eluted product was the starting 2-acetylpyrrole (5.5 g, 32.4%) mp.89-90°C. The second eluted product was 2,5-diacetylpyrrole (3.81 g, 16.2%), mp.158-159°C. Recrystallization from water-ethanol and dry nitromethane afford colorless needles, mp.160-160.5°C. IR (KBr) 3309 (NH s), 3108 (CH sh), 1662, 1648 (CH₃CO), 1538, 1427, 1360, and 1252 cm⁻¹; ¹HNMR (CDCl₃): δ 9.94 (br s, 1H, H-1), 6.86 (d, 2H, H-3, H-4), and 2.49 (s, 6H, CH₃). Anal. Calcd for C₈H₉NO₂: C, 63.57; H, 6.00; N, 9.27; O, 21.16. Found: C, 63.75; H, 5.94; N, 9.13; O, 21.18.

The third eluted product was 2,4-diacetylpyrrole (10.6 g, 45.1%), mp.137-138°C. Two recrystallization from petroleum-THF, mp. 139.5-140°C. IR (KBr) 3178 (NH s), 2981 (CH w), 1662, 1643 (CH₃CO), 1556, 1497, 1440, 1381, 1284, 1217, 1156, 946, 935, and 843 cm⁻¹; ¹HNMR (CDCl₃): δ 9.71(br s, 1H, H-1), 7.59 (two overlapping d, 1H, H-5), 7.26-7.30 (d, 1H, H-3), 2.48 (s, 3H, CH₃CO), and 2.46 (s, 3H, CH₃CO). Anal. Calcd for C₈H₉NO₂: C, 63.57; H, 6.00; N, 9.27; O, 21.16. Found: C, 63.59; H, 6.03; N, 8.99; O, 21.39.

Polymerization The procedure of Polymerization for poly (2,2'-(2,5-pyrrolyl)-4,4'-(*p,p'*-oxydiphenylene)bisquinoline) PAo is taken as an example. A solution of 6.64 g of di-*m*-cresyl phosphate (DCP) and 2.23 g of freshly distilled *m*-cresol was added to equimolar amounts (0.9925 mmol) of both A (0.4054 g) and o (0.1500 g) in a cylindrical-shaped reaction flask fitted with a mechanical stirrer, two gas inlets, and a side arm. The reactor was purged with argon for 5-10 min, before the temperature was raised to 135-140°C in about 30 min. As the viscosity of the reaction mixture increased with time, small amounts of *m*-cresol were added to the reaction mixture to facilitate efficient stirring. The reaction was maintained at this temperature for 68 h under static argon. After cooling, the resulting viscous solution was added dropwise into an agitated solution of 450 mL of ethanol containing 10% v/v of triethylamine. The precipitated polymer was then chopped in a blender and collected by suction filtration. The polymer was purified by continuous extraction in a Soxhlet extractor for 24 h with a ethanol solution contain 15% v/v triethylamine and dried at 100°C under vacuum for 24 h to afford 0.4441g (92%) of pure polymer. IR (KBr, cm⁻¹): 3436 (M(N-H)), 3060 (M(C-H)), 1592 (M(C-C)), 1543 (M(C-N)), 1492 (M(C-C)), 1424, 1393, 1348, 1231 (M(C-O)), 1205, 1167, 1101, 1014, 835 (δ (C-H)), 761, 711, 595, 572 (δ (C-H)). Tg = 325°C, thermal stability: 5% weight loss up to 536°C (10°C/min, air flow). Intrinsic viscosity [η] = 1.10 dL/g (solution in *m*-cresol, at 30°C).

Results and Discussion

Monomers Two diacetyl aromatic monomers, 2,5-diacetylpyrrole (o) and 2,4-diacetylpyrrole (m), were synthesized from 2-acetylpyrrole (3). 3 were prepared by two different path ways. One

synthetic method involved the direct acetylation of pyrrole with acetic anhydride under high-temperature pressure conditions to give a 38–40% yield of 3.¹⁰ But it was difficult to separate 3 from the reaction mixture of stick gum to suitable purity for next reaction and polymerization. Another synthetic scheme that requires the protection of pyrrole hydrogen with p-tolylsulfonyl is outlined in scheme 2.

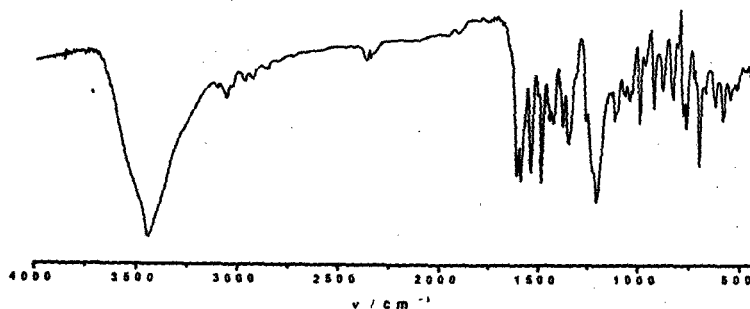
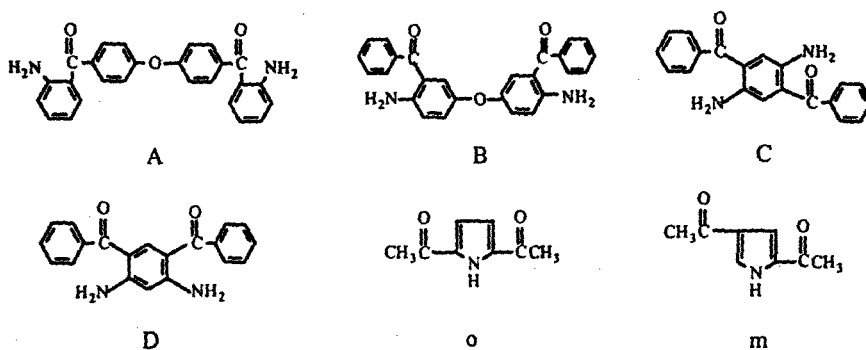
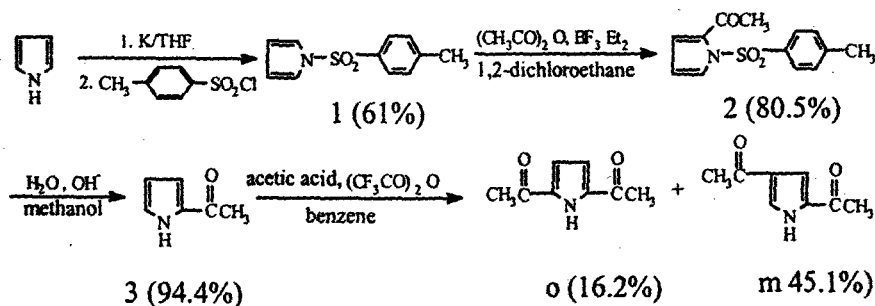


Figure 1 Infrared spectrum of PBo



Scheme 1 Monomers

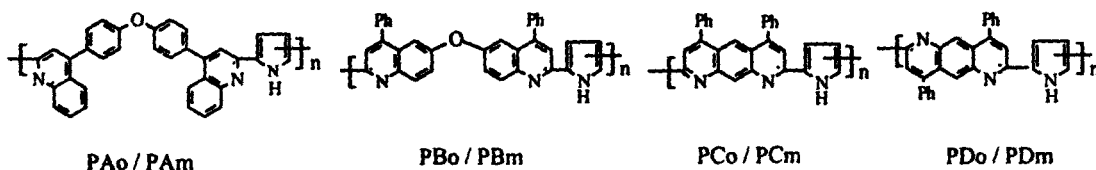


Scheme 2 Synthesis of Monomers B, o and m

Polymers The polymers containing quinoline and anthrazoline units were synthesized successfully using an equimolar mixture of the appropriate bis(o-aminoketone) (A,B,C,D) and diacetyl monomers (o,m) in good yield (see Table 1). Their structures, which were characterized by IR and Elemental analysis, were sketched in Scheme 3 and denoted by P followed the letters indicating the monomers used (hence, PAo, PAm, PBo, PBm, PCo, PCm, PDo, PDm). They comprised two groups of isomers (polyquinoline group and polyanthrazoline group), each group was composed of two couples of isomers.

Thermal properties Thermal properties of these polymers were summarized in Table 1. DSC measurement gave the glass transition temperatures of the polymers in the range 242–339°C and

TGA showed high thermal stability with the onset of decomposition between 514-554 °C in N₂.



Scheme 3 Polyquinolines and Polyanthrazolines

T_g or T_d of the polyquinolines (PAo, PAm, PBo, PBm) were higher than that of the polyanthrazolines (PCo, PCm, PDo, PDm) in N₂ but the decomposition temperatures of the polymers usually was lower in air than in N₂. The polymers with monomer m (PAm, PBm, PCm, PDm) were easy decomposition compared with their respective isomers that have same bisaminoketone structure (PAo, PBo, PCo, PDo) at T_{5%}. Moreover, compared the T_d of the polymers between each couple of isomers, it was found that PAo, PAm and PBo, PBm are similar but PDo, PDm have higher decomposition temperatures than PCo, PCm.

Solubility From the solubility shown in Table 1, it was found a progressive increase order for the solubility of polymers: polyanthrazolines < PAo < PBo < PAm < PBm. That could be attributed to difference of molecular structures. As the rigid-rod polyquinolines reported^{1,2}, polyanthrazolines without flexible linkage in back-bone displayed insolubility in all tested solvents; PBm, which with some favorable factors for enhancing the solubility of the polymers, such as flexible group in back-bone, pendent phenyl side group, extended chain conformation and easy solvation, was the easiest soluble in the series of polymers, the other polyquinolines were partially soluble (PS), but the polyquinolines all could dissolve in m-cresol and were spun into thin film on fused silica substrates while polyanthrazolines only dissolved in DCP/m-cresol solvent to be spun into thin film.

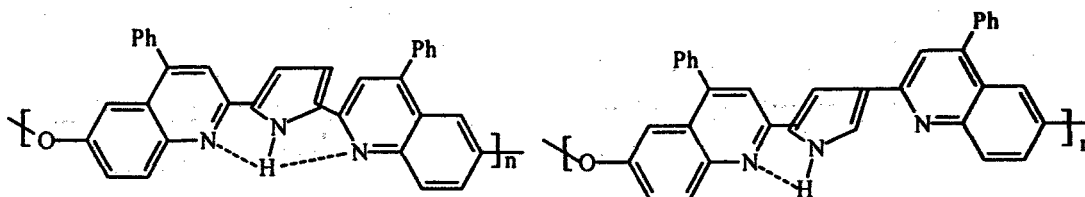
Table 1 Properties of Polyquinolines and Polyanthrazolines

polymer	Yield (%)	T _g ^a (°C)	T _d ^b (°C)			[η] ^c (dL/g)	Solubility		
			air	N ₂	T _{5%} in air		CH ₂ Cl ₂	DMA	m-Cresol
PAo	92	325	542	554	536	1.10	I	PS	S
PAm	91	339	539	544	483	0.59	PS	S	S
PBo	97	332	540	544	520	0.76	PS	PS	S
PBm	98	319	536	542	455	1.14	S	S	S
PCo	68	253	505	514	409	0.36	I	I	PS
PCm	84	281	520	528	398	0.95	I	I	PS
PDo	95	284	538	539	507	1.18	I	I	PS
PDm	96	242	535	536	478	1.11	I	I	PS

^a DSC, second heating, 10 °C/min, nitrogen flow. ^b TGA, onset of decomposition, 10 °C/min. ^c Intrinsic viscosity in m-cresol (PAo, PAm, PBo, PBm) and in 2wt%DCP/ m-cresol (PCo, PCm, PDo, PDm), at 30 °C.

Optical properties Some absorption spectra of thin films and solutions of the polymers are shown in Figure 2,3. Some important optical properties of all polymers are compiled in Table 2 for easy comparison. PDb⁹ and PDs⁹ were poly(1,6-anthrazolines) with 1,4-phenylene linkage and 2,5-thiophene linkage respectively. The maximum absorption wavelengths (λ^{*}_{max}) of thin films of polyquinolines and polyanthrazolines were located in 376-439 nm and 468-565 nm, these regions were identical with that of polyquinolines and polyanthrazolines with 2,5-thiophene linkage respectively. The fact proved that replacement of the phenylene linkage with the pyrrole linkage could produce a similar effect as that with thiophene linkage.⁹ However, correspondently

compared with 2,4- pyrrole linkage polymers (PAm, PBm PCm and PDm), the 2,5- pyrrole linkage polymers (PAo, PBo, PCo and PDo) have higher $\lambda_{\text{max}}^{\text{a}}$ values by about 46, 43, 92, 90 nm and smaller band gaps by $\sim 0.1\sim 0.3$ eV. These results showed that introduced 2,4- pyrrole linkage in main chain, which was a better linkage in reducing the steric hindrance than 2,5-pyrrole linkage, make $\lambda_{\text{max}}^{\text{a}}$ not to be increased but decreased, which illustrated that reducing the steric hindrance between two adjacent aromatic rings for coplane was not a effective way to enhance the conjugated electron delocalization in these sample, while the steric hydrogen bonds between quinoline N and pyrrole H was an important way to tend coplane of aromatic rings in the polymers (see Scheme 4). In addition, a red shift of about 67 nm in $\lambda_{\text{max}}^{\text{a}}$ and a smaller band gap by ~ 0.2



Scheme 4 The Conformations of the Steric Hydrogen Bonds in PBo and PBm

eV can be observed in PDo with 2,5-pyrrole linkage compared to PDs with 2,5-thiophene linkage, which also proved the effect of the steric hydrogen bonds. Polyanthrazolines exhibited higher $\lambda_{\text{max}}^{\text{a}}$ values by about 20~190 nm and smaller bands gaps by about 0.5~1.0 eV than the polyquinolines, that could be attributed to large extent of π -electron delocalization in the fully conjugated molecule of polyanthrazolines with 3 fused rings.

Table 2 The Optical Properties of Polyquinolines and Polyanthrazolines

Polymers	$\lambda_{\text{max}}^{\text{a}}$ (film) nm	E g (film) eV	$\lambda_{\text{max}}^{\text{a}}$ (soln) nm	$\lambda_{\text{max}}^{\text{e}}$ (soln) nm	Log ϵ
PAo	422	2.76	468	532	4.99
PAm	376	2.98	426	500	4.85
PBo	439	2.67	497	561	4.69
PBm	396	2.92	449	507	4.78
PCo	570	1.87	660	725	4.89
PCm	468	2.15	560	607	4.89
PDo	565	1.87	653	709	4.88
PDm	475	2.09	562	608	4.95
PDb*	443	2.47	442		4.49
PDs*	498	2.17	572		4.49

All spectra examined in 0.2% wt DCP/m-cresol. * The data from the literature.⁹ ϵ - molar absorption coefficient.

Since some effects of intermolecular interactions on the polymer chain conformations are negligible in solution, the effects of the pyrrol-structures were expected to be more evident in the solution spectra than in thin-film spectra. Table 2 lists the values for $\lambda_{\text{max}}^{\text{a}}$ in the solution spectra for the polymers. As can be seen, the order of increasing $\lambda_{\text{max}}^{\text{a}}$ and, hence, the order of increasing π -electron delocalization is: PAm < PBm < PAo < PBo < PCm < PDm < PDo < PCo, which is the same order as that observed in the solid-state spectra.

The maximum emission wavelengths ($\lambda_{\text{max}}^{\text{e}}$) of the polymers are shown in Table 2. There is a same order as their $\lambda_{\text{max}}^{\text{a}}$ of thin films and solutions. Their emission colors of the polymers could be turned from green (PAm, PBm) to yellow (PAo PBo), orange (PCm, PDm), and red (PDo,

PCo). By comparing the λ_{\max}^a and λ_{\max}^e of the polymers in solution, it could be seen that polymers have Stokes shifts of 45~75 nm, which is characteristic of excimer emission of many conjugated polymers⁹.

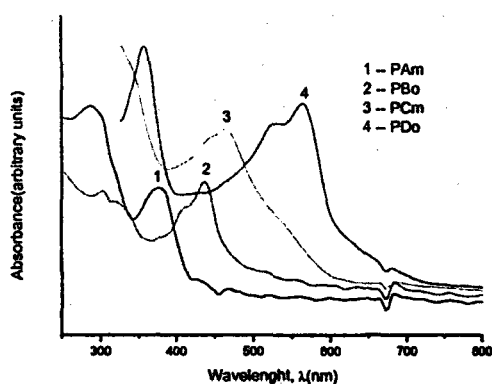


Figure 2 Optical absorption spectra of thin film of PAm, PBo, PCm, and PDo.

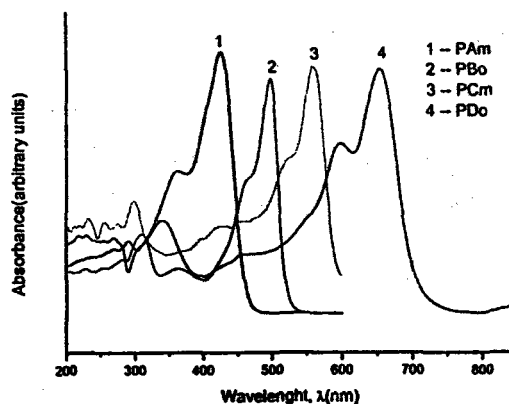


Figure 3 Optical absorption spectra of PAm, PBo, PCm, and PDo in solution (2wt%DCP/ m-cresol).

Conclusions

A series of 8 new polyquinolines and polyanthrazolines with pyrrole isomeric units in main chain were synthesized and characterized. The new polymers showed high thermal stability, and some of them were soluble in common organic solvents. The polymers with monomer o structure exhibited higher Td, lower Solubility, and higher λ_{\max}^a and λ_{\max}^e than their respective isomers with m structure, which was attributed to the effects of the more steric hydrogen bonds between quinoline N and pyrrole H in the molecule of the polymers with monomer o structure.

References

1. Stille, J. K. *Macromolecules* 1981, 14, 870-880.
2. Sutherland, D. M.; Stille, J.K. *Macromolecules* 1985, 18, 2669-2675.
3. Alam, M. M.; Jenekhe, S. A. *J. Phys. Chem. B* 2001, 105, 2479-2482.
4. Jen, A. K-Y.; Wu, X. M.; Ma, H. *Chem. Mater.* 1998, 10, 471-473.
5. Hou, S. F.; Jiang, J. Y.; Ding, M. X.; Gao, L. X. *Chemical Journal of Chinese Universities* 2002, 23(3), 480-489.
6. Imai, Y.; Johnson, E.F.; Katto, T.; Kurihara, M.; Stille, J. K. *J. Polym. Sci., Polym. Chem. Ed.* 1975, 13, 2233-2249.
7. Wolfe, J. F.; Stille, J.K. *Macromolecules* 1976, 9, 489-496.
8. Norris, S.O.; Stille, J. K. *Macromolecules* 1976, 9, 496-505.
9. Agrawal, A. K.; Jenekhe, S. A. *Macromolecules* 1993, 26, 895-905.
10. Ciamician, G. L.; Silber, p. *idid*, 1885, 15, 9.