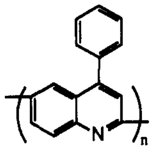
New Conjugated Polyanthrazolines Containing Thiophene Moieties in the Main Chain

Conjugated polymers are in the forefront of research on electronic and nonlinear optical materials.[1-3] Although many conjugated polymers have been investigated, their electronic and nonlinear optical properties are not ideal. Therefore, there is a continuing search for new conjugated polymers that might combine all the important properties like thermal stability, mechanical strength, and large nonlinear optical properties or high conductivity. One promising class of conjugated polymers, namely rigid-rod polyquinolines/polyanthrazolines, was recently investigated by us for the purpose of elucidating structure–nonlinear optics ($\chi^{(3)}$) relationships in polymers.[4] These phenylated polyquinolines/polyanthrazolines, for example, **1**, **2a**, **3a**, and many others, first synthesized by Stille and co-workers,[5-7,14-16] exhibit high thermal stability (>550 °C),[6] excellent mechanical properties,[7] good linear optical properties, including low optical losses (1–10 cm^{-1}) in the transparent region (800–3000 nm) and high refractive indices (1.6–2.0),[8] and large photoconductivity.[9] However, their electronic and third-order nonlinear optical properties were found to be essentially similar to those of many other classes of conjugated polymers. These polymers could only be n-type doped to give moderate conductivities of about 10 S/cm.[10] Picosecond third harmonic generation (THG) measurement of the third-order nonlinear optical properties of these polyquinolines in the wavelength range of 0.8–2.4 μm gave a nonresonant $\chi^{(3)}$ (-3ω; ω, ω, ω) value of $\sim 2 \times 10^{-12}$ esu and a three-photon resonant value of $\sim 10^{-11}$ esu.[4] One of the main reasons for the small $\chi^{(3)}$ values, among others, may be the poor π-electron delocalization along the backbone of the polymer chain which also gives these polymers their yellow to orange color (λ_{max} $\sim$394–414 nm) and large band gaps of 2.81–2.56 eV.[8] Therefore, if significant improvements in the electronic structure could be made, these polymers may show promise as new third-order nonlinear optical materials with improved optical nonlinearities. The electrical and photoconductive properties may also be improved by the electronic structure modification.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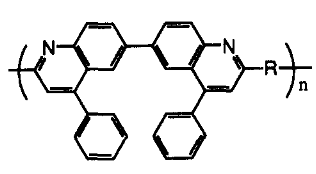
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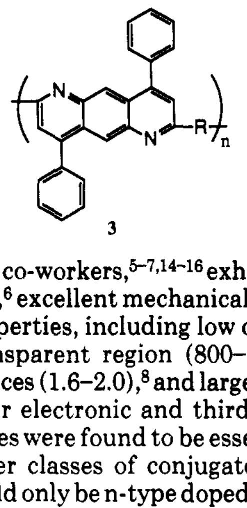
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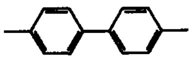
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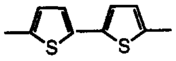
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In this paper we report the synthesis and characterization of a new monomer and two new polymers, poly(2,7-(2,2′-bithiopheneyl)-4,9-diphenyl-1,6-anthrazoline) (PBTDA, **3b**) and poly(2,7-(2-thienylethynyl-2-thienyl)-4,9-diphenyl-1,6-anthrazoline) (PBTADA, **3c**), in the class of polyquinolines/polyanthrazolines (**1**–**3**). These bithiophene-linked polymers were designed to modify the electronic structure and optical properties of the known *p*-biphenylene-linked polymer, poly(2,7-(*p*,*p*′-biphenylyl)-4,9-diphenyl-1,6-anthrazoline) (PBDA, **3a**). Polymers containing thiophene moieties in the main chain were recently synthesized in our laboratory,[11] and our previous studies of conjugated polythiophenes showed them to exhibit large $\chi^{(3)}$ values.[3e,f] Also, recently, it was reported by Prasad et al.[12] that replacement of a benzene ring with a thiophene ring in benzothiazole, benzoxazole, and benzimidazole small molecules resulted in an increase of the second hyperpolarizability γ. It was proposed that the thiophene ring places significantly less steric hinderance compared to benzene rings, thereby permitting a greater degree of π-electron delocalization, and the thiophene ring possesses a highly polarizable sulfur atom which increases the overall π-electron density in the system. Also, the "d" orbitals of the sulfur atom mix favorably with the π orbitals of the conjugated carbon backbone.[12c]

Monomer Synthesis. 5-Acetyl-2-aminobenzophenone,[13] 3,3′-dibenzoylbenzidine,[7,14] 2,5-dibenzoyl-1,4-phenylenediamine,[15] and di-*m*-cresyl phosphate (DCP) (reaction medium)[16] were prepared according to the methods described in the literature. 4,4′-Diacetylbiphenyl was obtained from Aldrich and recrystallized from methanol. All starting materials were obtained from Aldrich and were used as received.

5,5′-Diacetyl-2,2′-bithiophene was synthesized using the method of Wynberg and Logothetis[17] and was further purified by recrystallization from ethyl alcohol: mp 233.5 °C (lit. mp 233.5–234 °C); UV/vis ($CHCl_3$) λ_{max} 367 (log ϵ = 4.19), 262 (3.57); IR (Nujol, cm^{-1}) 3060, 1660, 1440, 1370, 1310, 1280, 1040, 945, 905, 890, 800; ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 7.59 (d, 2 H), 7.28 (d, 2 H) 2.55 (s, 6 H).

1,2-Bis(5-acetyl-2-thienyl)acetylene (BATA): A solution of 12.3 g (60 mmol) of 2-acetyl-5-bromothiophene (99%) and 1.45 g (1.25 mmol) of tetrakis(triphenylphosphine)palladium(0) in 75 mL of dry THF was added to a solution of 15 g (25 mmol) of bis(tri-*n*-butylstannyl)acetylene in 25 mL of THF (dry) under an inert atmosphere. The resulting dark brown solution was heated to reflux under an argon blanket for 60 h. Thereafter, it was slowly cooled down to room temperature and then to −10 °C, during which time fine greenish needlelike crystals of product were formed. The product was removed by suction filtration (1.5 g; 21.9% yield). The product was purified by recrystallization from a THF–hexane (9:1) mixture to give 1.4 g of greenish yellow small needlelike crystals: mp 214 °C; UV/vis ($CHCl_3$) λ_{max} 387 (log ϵ = 4.25), 362 (4.31), 281 (3.78); IR (Nujol, cm^{-1}) 3070, 1670, 1390, 1295, 1260, 1045, 945, 910, 820; ^{1}H NMR (CD_2Cl_2, 300 MHz, TMS) δ 7.60 (d, 2 H), 7.33 (d, 2 H), 2.55 (s, 6 H); ^{13}C NMR (CD_2Cl_2, 300 MHz, TMS) δ 189.9, 145.9, 133.5, 132.1, 129.3, 88.6, 26.5. Anal. Calcd for $C_{14}H_{10}O_2S_2$: C, 61.29; H, 3.67. Found: C, 61.09; H, 3.50.

Polymer Synthesis. Polymer **3a** was synthesized according to the literature procedure.[15] However, DCP/*m*-cresol was used as the reaction medium for the polymerization to achieve high molecular weight polymer.[16] The new polymers PBTDA (**3b**) and PBTADA (**3c**) were synthesized as follows.

PBTDA (3b). Equimolar amounts of both 2,5-dibenzoyl-1,4-phenylenediamine (0.5 g) and 5,5′-diacetyl-2,2′-bithiophene (0.3957 g) were added along with 15 g of

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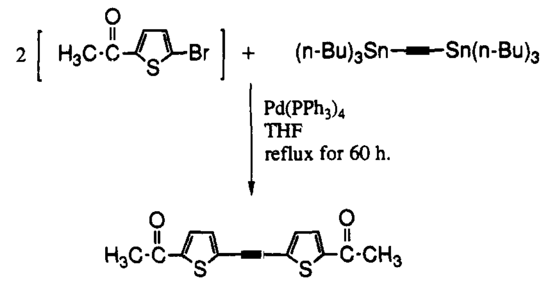
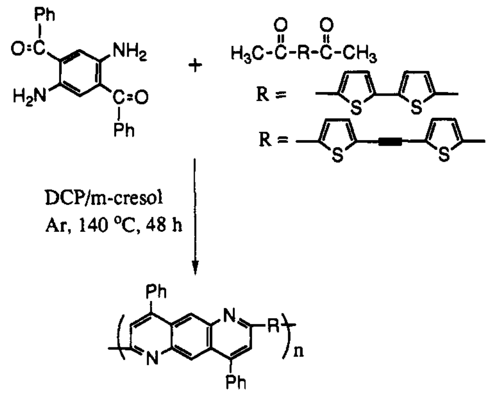
Scheme I



Scheme II



diphenyl phosphate (DPP) and 2 g of freshly distilled *m*-cresol in a glass reactor fitted with mechanical stirrer, two gas inlets, and a side arm. The reaction mixture was purged with Ar for 15 min, and then the temperature was raised to 140 °C under positive pressure of Ar. The temperature was maintained for 48 h, during which time small amounts of *m*-cresol were added to facilitate efficient stirring of the reaction mixture whenever it became highly viscous. After cooling, the polymerization dope was slowly poured into a stirred solution of 500 mL of ethanol/50 mL of triethylamine (TEA). The precipitated polymer was then chopped in a blender and collected by suction filtration. The polymer was purified by continuously extracting it with 20% TEA/ethanol solution for 24–36 h and was dried in vacuum at 80 °C: $[\eta] = 2.3$ dL/g (25 °C, 1.5 mol % DCP/*m*-cresol); IR (free-standing film, cm^{-1}) 3055, 2964, 1588, 1527, 1492, 1442, 1425, 1358, 1274, 1232, 1074, 1030, 892, 794, 765, 700, 613, 546. Anal. Calcd for $(C_{32}H_{18}N_2S_2)_n$: C, 77.7; H, 3.67; N, 5.66. Found: C, 75.76; H, 3.59; N, 5.34.

PBTADA (3c). It was prepared using equimolar amounts of 2,5-dibenzoyl-1,4-phenylenediamine (0.5 g) and 1,2-bis(5-acetyl-2-thienyl)acetylene (0.4336 g) in di-*m*-cresyl phosphate (DCP) as the solvent medium instead of DPP. The same procedure as described above was used for the polymerization: $[\eta] = 4.4$ dL/g (25 °C, 0.1 mol % DCP/*m*-cresol); IR (free-standing film, cm^{-1}) 3055, 2971, 1589, 1530, 1492, 1445, 1427, 1355, 1290, 1240, 1063, 1030, 894, 807, 766, 701, 614, 546. Anal. Calcd for $(C_{34}H_{18}N_2S_2)_n$: C, 78.74; H, 3.50; N, 5.40. Found: C, 76.82; H, 4.03; N, 4.66.

Results. The new monomer BATA was successfully synthesized using Scheme I and characterized. The low yield obtained may be due to the poor quality of the catalyst used. The new polymers **3b** and **3c** were successfully synthesized using Scheme II and characterized by Fourier transform infrared (FT-IR) and UV–vis spectroscopy, intrinsic viscosity, thermogravimetric analysis (TGA), and elemental analysis. The new polymers were obtained in essentially quantitative yield (>95%), with high intrinsic viscosity and high thermal stability (Table I). The somewhat lower decomposition temperature of PBTADA compared to the other two polymers may be attributable to the lower thermal stability of the bithienylacetylene linkage. Disappearance of carbonyl absorption bands of the monomers and appearance of new strong bands between 1600 and 1400 cm^{-1} in the FT-IR spectra of the polymers confirmed the completion of a cyclization reaction to form the anthrazoline rings. A small difference in the elemental analyses was observed, and this is similar to that obtained for other polyanthrazolines by Imai et al.[15] It is characteristic of thermally stable polymers with a high percentage of carbon to give lower experimental values by 1–2 wt %. The new polymers (**3b**, **3c**), which are deep red to purple under transmission of light, had a metallic luster in solid form under reflection and could be easily solubilized in organic solvents using the complexation-mediated solubilization[8] in DCP/*m*-cresol, DPP/*m*-cresol, or $GaCl_3$/nitromethane. Furthermore, free-standing as well as spin-coated thin films of the pure polymers on substrates could be easily casted from the solutions using methods similar to those described elsewhere[8] for a series of rigid-rod polyquinolines. The polymer films were shown to be free of the complexing species DCP, DPP, or $GaCl_3$ by thermal analysis and spectroscopic techniques.

Table I
Properties of Conjugated Polyanthrazolines

polymer	$[\eta]$, dL/g	thermal stability[a]	λ_{max}(film), nm	E_g(film), eV	λ_{max}(soln),[b] nm	log ϵ
PBDA	6.85	600	414	2.56	484	4.67
PBTDA	2.3	600	520	2.07	659	4.90
PBTADA	4.4	415	525	2.0	709	4.72

[a] Onset point (in °C) determined by TGA in N_2 at the rate of 10 °C/min. [b] Solutions made in DCP/*m*-cresol.

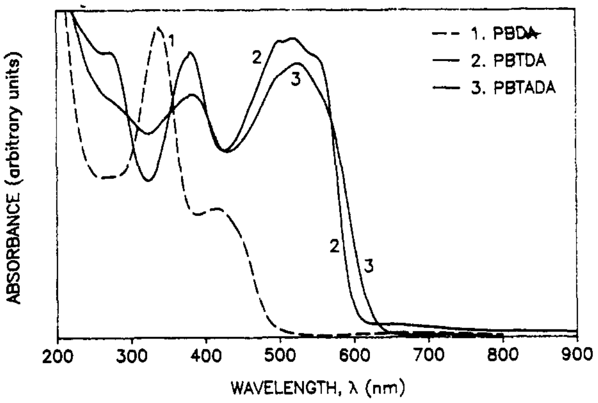


Figure 1. Optical absorption spectra of thin films of PBDA, PBTDA, and PBTADA.

The optical absorption spectra of thin films of polymers PBTDA (**3b**) and PBTADA (**3c**) are shown in comparison to that of PBDA (**3a**) in Figure 1. As can be seen from Figure 1 and Table I, the replacement of the biphenyl linkage with a bithiophene linkage has resulted in a significant red shift of λ_{max} by about 105 nm and a reduction of the optical band gap from 2.56 eV in PBDA to 2.07 eV in PBTDA. The changes are even greater when a bithienylacetylene linkage is introduced as in PBTADA. In this case, the optical band gap is further reduced to 2.0 eV. If PBTDA was to be considered as an alternating copolymer formed from the additive contributions of segments of the two homopolymers poly(2,6-(4-phenylquinoline)) (PPQ, **1**) and polythiophene, then these optical properties would be expected to fall in between those of the two constituent homopolymers. However, this is not the case. The λ_{max} and band gap of pure poly(2,5-thiophenediyl) are typically 480–500 nm and 2.0 eV, respectively.[18] The band gap and

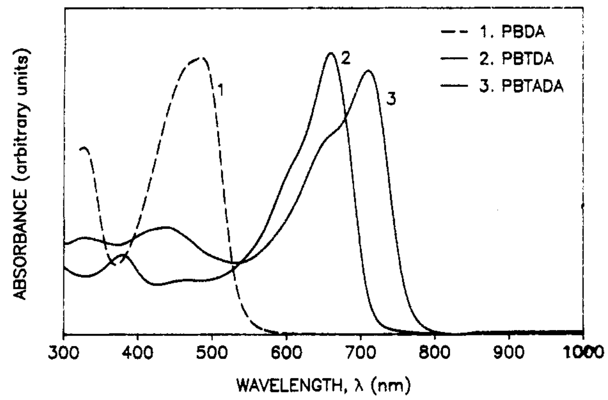


Figure 2. Optical absorption spectra of solutions of PBDA, PBTDA, and PBTADA in 0.1–1.5 mol % DCP/*m*-cresol.

λ_{max} of the optical absorption spectrum of PBTDA lie very close or superior to those of the pure polythiophene which suggests that the electronic identity of the individual subunits is lost and an overall new electronic structure has evolved as a result of the modification in the molecular structure.

Another noticeable difference in the optical absorption spectra is the higher strength of the lowest energy π–π^* transitions relative to other transitions in PBTDA and PBTADA in contrast to PBDA, which shows a much weaker lowest energy transition. This might favorably affect the magnitude of the lowest order transition dipole moment, which according to our recent studies seems to play a key role in obtaining large third-order nonlinear optical properties.[19]

The solution optical spectra of the polymers in 0.1–1.5 mol % DCP/*m*-cresol (Figure 2) again show trends which are similar to those seen in the solid-state spectra. However, the changes from the biphenylene to the bithiophene linkage are much more dramatic in the solution spectra. There is a red shift of λ_{max} of the polymers by 175 nm from PBDA to PBTDA and by 225 nm from PBDA to PBTADA. Also, the λ_{max} of the polymers in solution phase are red shifted by large values compared to the respective λ_{max} in the solid-state spectra. These solution spectra results are due to acid–base complexation of the polymers by DCP at the nitrogen sites in the polymers which results in a much more planar conformation of the protonated polymer chains.[8,20]

In summary, we have synthesized and characterized two new conjugated polyanthrazolines (PBTDA, PBTADA) containing 2,2′-bithiophene and 2,2′-bithienylacetylene linkages. The new polymers showed significant changes in electronic structures as evidenced by the large variations in the linear optical properties compared to the *p*-biphenylene-linked polymer (PBDA). With these modifications in the molecular structure of the polyanthrazolines, polymers with smaller band gaps (~2 eV) were realized in this class of conjugated polymers. It is expected that these polymers may show improved nonlinear optical, electronic, and photoconductive properties. Studies of these properties are in progress and will be reported in the future. If polymers **3b** and **3c** are thought of as derivatives of conjugated polythiophenes, instead of as polyanthrazolines, then they are high strength, thermally stable, and solution-processable derivatives without the drawbacks of long side-chain substitutions which are generally used to solubilize polythiophenes.

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