

Communications to the Editor

Stereoregular Poly(benzoquinone imines) from Methyl-Substituted Benzoquinones

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Introduction. Polyaniline, prepared by chemical or electrochemical oxidation of aniline, has attracted much interest due to its remarkable electrical, electrooptical, and tensile properties.^{1,2} A *polycondensation* route to polyanilines is a desirable synthetic alternative to the nondiscriminating oxidative polymerization. It would allow the use of a wide variety of monomers and also give a clean, well-defined polymer. Several groups had investigated polycondensation routes to polyaniline and its analogs, but they do not provide an easy pathway for derivatization.³ A condensation of the parent benzoquinone BQ with 1,4-phenylenediamine PDA using poly(phosphoric acid) was reported by Uehara in the 1970s.⁴ We have been unable to repeat these claims. After extensive studies it was determined that a nucleophilic Michael attack predominates over the desired carbonyl condensation. The undesirable Michael side reaction has therefore eliminated BQ from consideration as a comonomer in our studies. Thus far only anthraquinones and heterocyclic quinones, in which all possible Michael positions are substituted, have been successfully used as comonomers in diimine formation.⁵

In a continuing effort to synthesize analogs of polyaniline and to have more control over the structure of the obtained polymer, partially substituted benzoquinones have now been investigated as monomers using the $\text{TiCl}_4/\text{DABCO}$ procedure developed in these laboratories.⁵ Model reactions with monofunctional amines will be performed. We have previously shown that the structure of the model compound is a good indication for the polymer structure.⁵ We will show that the stereoregular structure of the polymer can be controlled by the substitution pattern of the quinone monomers.

Results and Discussion. Model Studies. The structure of the model diimines of the following substituted quinones will be investigated: 2,5-dimethylbenzoquinone, 25BQ; 2,6-dimethylbenzoquinone, 26BQ; and 2,3,5,6-tetramethylbenzoquinone (duroquinone), DQ. *N,N*-Diphenylbenzoquinone diimines were synthesized in one-step reactions from these methyl-substituted benzoquinone derivatives. 25BQ, 26BQ, and DQ were allowed to react with 2 equiv of aniline in the presence of TiCl_4 and DABCO to give the corresponding *N,N*-diphenyl diimines, as shown in Scheme 1. The model compounds *N,N*-diphenyl-(2,5-dimethylbenzoquinone) 1,4-diimine, 25DBQI, and *N,N*-diphenyl-duroquinone 1,4-diimine, DQI, were isolated as red crystalline solids in yields of 69 and 70%, respectively, without optimization. *N,N*-Diphenyl-(2,6-dimethylbenzoquinone) 1,4-diimine, 26DBQI, was isolated as a dark red waxy solid

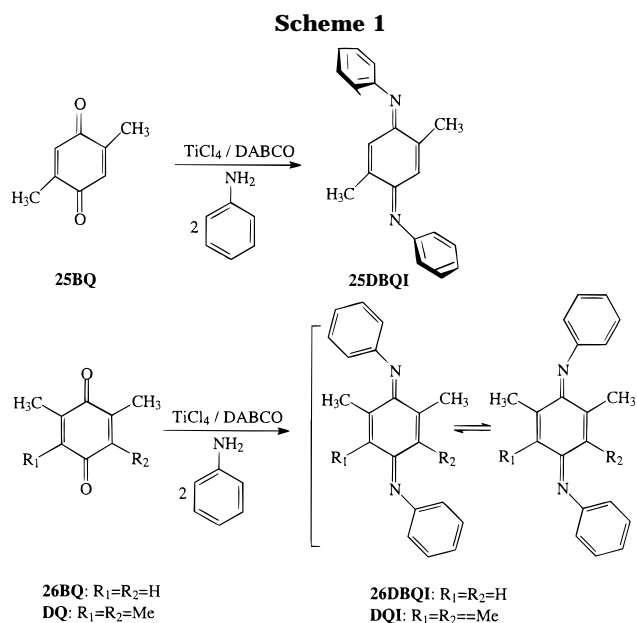


Table 1. Ultraviolet Data for Model Compounds and Polymers of Substituted Benzoquinones in Tetrahydrofuran

quinone	λ_{max} (nm)		
	model compound	SDA polymer (nm)	MDA polymer
25BQ	444	486	464
26BQ	438		
DQ	422		
AQ ^a	398	424	410

^a See ref 5 for experimental details.

in 70% yield. In order to obtain a crystalline compound, which could be purified by recrystallization and characterized by X-ray crystallography, the *p*-bromoaniline derivative, *N,N*-(4,4'-dibromodiphenyl-(2,6-dimethylbenzoquinone)) 1,4-diimine, Br26DBQI, was synthesized.

The observed red colors of the isolated *N,N*-diphenyl diimine model compounds indicate extended conjugation and delocalization of the π -electrons. The λ_{max} values for the benzoquinone diimines are shifted to longer wavelengths compared to the previously reported *N,N*-diphenylanthraquinone 9,10-diimine DAQ derivatives (DAQ λ_{max} = 398 nm),^{5a} as shown in Table 1. The anthraquinone diimines possess a buckled central ring system, which limits the amount of extended conjugation. The shifts for the reported BQ diimines are in agreement with similar *N,N*-diphenylbenzoquinone diimines.⁶ Honzl has reported that, with increasing chain length, the λ_{max} continues to shift to longer wavelengths, indicating delocalization of the electrons through the π -orbitals.⁷ Nakamura, however, has attributed the shift to longer wavelengths to the configurational interactions of the molecule, and not just a HOMO–LUMO energy gap change.⁸

The ambient temperature ¹H NMR spectrum of 25DBQI indicates that this *N,N*-diphenyl diimine ex-

clusively exists in the *anti* configuration, with the *N*-phenyl rings directed away from the methyl substituents. The methyl peak resonances occur as a sharp singlet at δ 2.09 ppm. The sharpness of the methyl peak indicates that no isomerization is occurring about the C=N bond of the *N*-phenyl imine. The aromatic region of the ^1H NMR spectrum is symmetrical, with only one set of *N*-phenyl imine peaks being observed, also indicating a single isomer.

Confirming this interpretation, X-ray crystallographic structure analysis of 25DBQI (Figure 1), shows that the *N*-phenyl rings are directed away from the methyl substituent in an *anti* configuration, as the solution state ^1H NMR predicted. The *N*-phenyl rings are twisted out of planarity with the central ring by 58° . The lack of coplanarity is also observed in most non-H-bonded *N*-benzylideneanilines, indicating that the phenyl ring prefers to be in conjugation with the nitrogen lone pairs and not in extended π -conjugation.⁹ The C1–N1 bond length is 1.294(4) Å and the C1–N1–C15 bond angle is $122.0(3)^\circ$ in agreement with accepted bond lengths and bond angles for imine functionalities.

In contrast to the sharp singlet methyl peak observed for 25DBQI in the ^1H NMR spectrum, the methyl signal of 26DBQI appears as two separate broad peaks at δ 1.6 and 2.5 ppm. Two distinct sets of *N*-phenyl imine peaks can also be observed. The broadness of the two sets of peaks indicates rapid isomerization about the C=N bond.

The ^1H NMR spectra of DQI revealed two broad singlets for the methyl substituents, similar to 26DBQI. Again, the broadness of the methyl peaks indicates that the imine is isomerizing quite readily at room temperature in solution. A variable-temperature NMR experiment was performed on DQI. When DQI was heated to 323 K, the two peaks coalesced, corresponding to an energy barrier for imine isomerization of 15.2 kcal/mol, as calculated from the Eyring equation.¹⁰ This is about 2 kcal/mol less than the isomerization barrier observed for the *N,N*-diphenyl diimine model compound DAQ.^{5d} These energy barriers fall well within the reported range of 12–20 kcal/mol for various other imines.¹¹

Polymerization Studies. The high yields encouraged the hope that condensation polymerization should be successful. The model compound studies indicated that control of the stereochemistry could be achieved by the appropriate substitution pattern. A polymer incorporating 25BQ should preferentially exist in the *anti* configuration, while a polymer incorporating 26BQ or DQ will have no preference for either configuration. Since a stereoregular polymer microstructure would be obtained with 25BQ, all polymer studies to date have focused on this benzoquinone derivative.

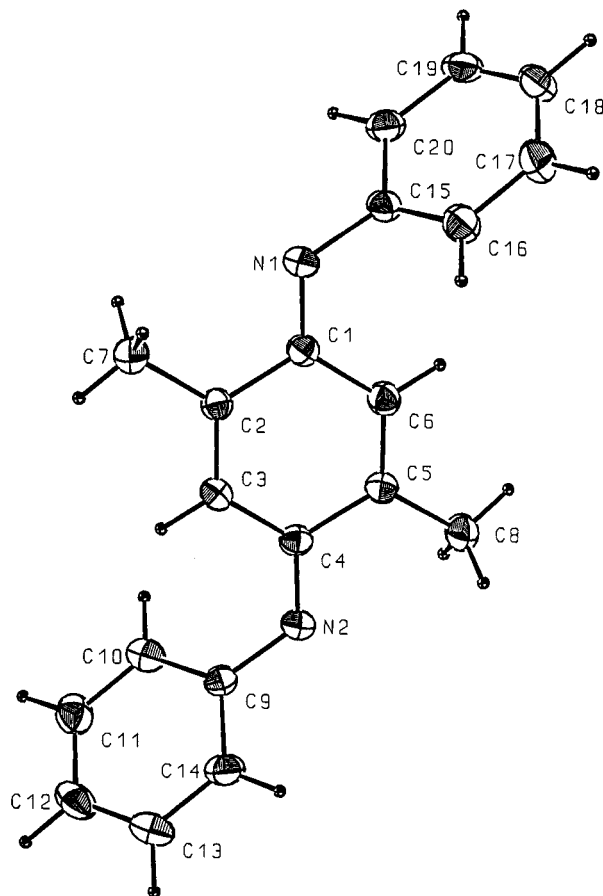
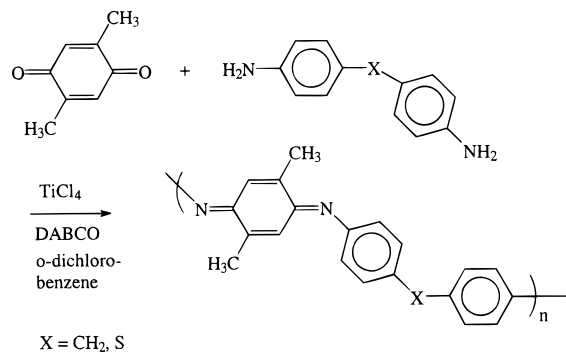


Figure 1. X-ray crystal structure of *N,N*-diphenyl-(2,5-dimethyl)benzoquinone 1,4-diimine (25DBQI).

Polymerizations of 25BQ were successfully carried out using both 4,4'-thiodianiline SDA and 4,4'-methylenedianiline MDA to yield moderately high molecular weight materials M_w 13 700, M_n 6 900 and M_w 30 200, M_n 12 200, respectively. Relative molecular weights of the polymers were determined by SEC. The 25BQ/MDA polyquinone imine forms free standing films which exhibit some structural strength. No mechanical testing has been performed on these polymer films. The 25BQ/SDA polyquinone imine does not easily form free standing films and was isolated as an amorphous solid. In the SEC we also observed a series of sharp low molecular weight peaks, with molecular weights ranging from \sim 600 to 2500. Similar oligomers have been previously observed in other polymerizations of aromatic diamines and quinone derivatives. In the case of methylenedianiline and anthraquinone, they were fully characterized by FAB-MS, and found to be cyclic dimers, trimers, tetramers, and pentamers.^{5b} For the MDA/25BQ and SDA/25BQ polymerizations, the macrocycles accounted for 6.9% and 4.0% of the high molecular weight material, respectively.

These polybenzoquinone imines incorporating SDA and MDA are not fully conjugated due to the spacer linkages, but do have structural similarities to the pernigraniline form of polyaniline. The 25BQ/SDA absorption spectrum λ_{max} of 486 nm indicates that there is extended π -conjugation. This value can be compared to the λ_{max} of the AQ/SDA (424 nm) polyanthraquinone imine. The absorption spectrum λ_{max} of the AQ/SDA polymer is at 60 nm shorter wavelength, indicating much less extended π -conjugation. The differences between the AQ and 25BQ polyquinone imines can be

attributed to the buckled central ring system observed in the former, which limits the amount of actual π -overlap.

Attempts at incorporation of *p*-phenylenediamine PDA into the polymer backbone have thus far been unsuccessful because the obtained products were quite intractable. The polymer could not even be separated from the TiO_2 /DABCO salts by Soxhlet-extraction of the reaction product with dichlorobenzene. Insolubility and intractability are common problems associated with π -conjugated polymer systems. Pioneering work in solubilizing rodlike polymers by Wegner and co-workers¹² with 2,5-dialkyl-substituted phenylenediamines may be applicable to these polymer systems.

In this work we have successfully synthesized stereoregular benzoquinone imine polymers utilizing a polycondensation reaction. Investigations are continuing into the successful incorporation of PDA into the polymer backbone and determination of the polymers' physical properties. The polymers described in this work are getting closer in structure to the parent polyaniline. Incorporation of a conjugated solubilizing diamine with 25BQ should provide a soluble, well-defined conducting polymer.

Experimental Section. The same conditions and procedures previously described for obtaining *N,N*-diphenyl anthraquinonedimine model compounds and polyquinone imines were used to obtain the model compounds and polymers described in this paper.^{5b}

***N,N'*-Diphenyl-(2,5-dimethyl)benzoquinone 1,4-Diimine (25DBQI).** The product was isolated and repeatedly recrystallized from ethyl acetate. Yield, %: 69.4 (red crystals). Mp: 191–194 °C, ¹H-NMR, δ (CDCl_3 , 25 °C): 2.09 (s, 6H), 6.62 (s, 2H), 6.85 (d, 4H), 7.18 (t, 2H), 7.4 (t, 4H). ¹³C-NMR, δ (CDCl_3 , 25 °C): 29.6, 44.7, 120.0, 122.7, 124.2, 128.9, 143.7, 150.7, 159.5. IR (KBr): 2913, 1571 (C=N), 1479, 1264, 1051, 759, 697 cm^{-1} . MS, m/z (M^+ , 100) 286, 194, 182, 167, 77, 51. UV-vis: λ_{max} (THF) 444 nm, $\epsilon = 5600 \text{ M}^{-1} \text{ cm}^{-1}$. Anal. Calcd for $\text{C}_{20}\text{H}_{18}\text{N}_2$: C, 83.87; H, 6.34; N, 9.78%. Found: C, 83.82; H, 6.34; N, 9.89.

Polymerization of 2,5-Dimethylbenzoquinone (25BQ) and 4,4'-Thiodianiline. Yield, %: 75.7 (red solid), ¹H-NMR, δ (CDCl_3 , 25 °C): 2.13 (s, 6H) 6.66 (s, 2H), 6.81, (d, 4H), 7.37 (d, 4H).¹³ C-NMR, δ (CDCl_3 , 25 °C): 17.9, 121.2, 122.7, 131.4, 131.8, 144.0, 149.8, 159.1. IR (KBr): 3050, 2990, 1583 (C=N), 1475, 1260, 1081, 1008, 802 cm^{-1} . UV-vis: λ_{max} (THF) 486 nm, $\epsilon = 8000 \text{ M}^{-1} \text{ cm}^{-1}$. Anal. Calcd for $\text{C}_{20}\text{H}_{16}\text{N}_2\text{S}$: C, 75.92; H, 5.10; N, 8.85; S, 10.11. Found: C, 73.16; H, 4.85; N, 8.51.

Polymerization of 2,5-Dimethylbenzoquinone (25BQ) and 4,4'-Methylenedianiline. Yield, %: 45.7 (red solid), ¹H-NMR, δ (CDCl_3 , 25 °C): 2.05 (s, 6H), 3.06 (s, 2H), 6.62, (s, 2H), 6.71 (bs, 4H), 7.14 (bs, 4H). ¹³C-NMR, δ (CDCl_3 , 25 °C): 17.9, 42.8, 115.0, 120.5, 122.7,

129.6, 137.3, 143.7, 148.8, 158.9. IR (KBr): 2918, 1580 (C=N), 1506, 1265, 1105, 1008, 808 cm^{-1} . UV-vis: λ_{max} (CHCl_3) 464nm, $\epsilon = 150 \text{ M}^{-1} \text{ cm}^{-1}$. Anal. Calcd for $\text{C}_{21}\text{H}_{18}\text{N}_2$: C, 84.52; H, 6.09; N, 9.38%, Found: C, 82.73; H, 5.82; N, 11.14.

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Supporting Information Available: Text giving experimental results and figures showing crystallographic ¹H NMR spectra for 25DBQI, 26DBQI, and Br26DBQI and tables of experimental details, positional parameters, general displacement parameter expressions, bond distances and angles, least square planes, dihedral angles between planes, and torsional angles for 25DBQI (12 pages). Ordering information is given on any current masthead page.

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