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Novel Polyaromatic Quinone Imines. 2. Synthesis of Model Compounds and Stereoregular Poly(quinone imines) from Disubstituted Anthraquinones

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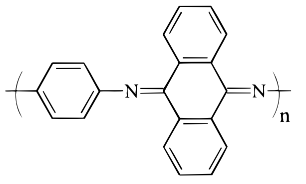
ABSTRACT: Novel poly(quinone diimines) from anthraquinones symmetrically disubstituted with solubilizing ethyleneoxy or long chain alkoxy groups have been synthesized and characterized. The disubstituted anthraquinones 1,5-bis(2-methoxyethoxy)anthraquinone (EO_1AQ), 1,5-bis(2-(2-methoxyethoxy)ethoxy)anthraquinone (EO_2AQ), 1,5-bis(2-(2-(2-methoxyethoxy)ethoxy)anthraquinone (EO_2AQ), 1,5-bis(2-(2-2-methoxyethoxy)ethoxy)ethoxy)anthraquinone (EO_3AQ), 1,5-bis(octyloxy)anthraquinone (15OOAQ), 2,6-bis(octyloxy)anthraquinone (26OOAQ), and 1,4-bis(octyloxy)anthraquinone (14OOAQ) were synthesized and condensed with aniline in the presence of titanium tetrachloride and 1,4-diazabicyclo[2.2.2]octane to give *N*,*N*′-diphenyl-1,5-bis(2-methoxyethoxy)$_n$anthraquinone 9,10-diimine (DEO_nAQ, $n = 1-3$), *N*,*N*-diphenyl-1,5-bis(octyloxy)anthraquinone 9,10-diimine (15DOOAQ), and *N*,*N*′-diphenyl-2,6-bis(octyloxy)anthraquinone 9,10-diimine (26DOOAQ), respectively, as model compounds for the polymers. The relative stereochemistry of these diimines was determined by ^{1}H NMR spectroscopy. Polycondensation of the disubstituted anthraquinones with 4,4′-thiodianiline (SDA) gave high molecular weight (M_w 30 000) poly(anthraquinone diimines) and large macrocycles. Polycondensation of 1,4-phenylenediamine (PDA) with EO_2AQ gave high molecular weight (M_w 14 000) polyaromatic anthraquinone diimines. PDA gave molecular weights of M_w 5000−23 000 for the bis(octyloxy)-substituted anthraquinones. The molecular weights of polymerizations incorporating PDA are lowered due to steric interactions of successive repeat units and solubility constraints.

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. An important step in this direction was described by Wudl and co-workers.[3,4] The condensation polymerization of 1,4-cyclohexanedione-2,5-dicarboxylic acid and an aromatic diamine was followed by a pyrolitic decarboxylation and partial dehydrogenation to yield the emeraldine form of polyaniline. The obtained polymer was identical to polyaniline made by the oxidative route, but this path was only used to synthesize the unsubstituted polyaniline.


PDA/AQ Poly(quinone imine)

A novel synthetic route to poly(quinone diimines) was recently developed in this laboratory.[5,6] The condensation polymerization of anthraquinone (AQ) with aromatic diamines in the presence of titanium tetrachloride and 1,4-diazabicyclo[2.2.2]octane (DABCO) as base in refluxing chloro- or *o*-dichlorobenzene led to polymers having molecular weights of M_w 15 000 and oligomeric macrocycles. AQ was polymerized with 4,4′-oxy(ODA) and 4,4′-thiodianiline (SDA), as well as with 1,4-phenylenediamine (PDA). The latter polymer is the dibenzo analog of the pernigraniline base form of polyaniline.

The solubility of polymers is always a critical factor in both characterization and processing. The molecular weight of the previously synthesized poly(quinone diimines) was believed to be constrained by their solubility. This has led us to investigate derivatized anthraquinones with solubilizing side chains attached in the 1,4-, 1,5-, and 2,6-positions. 1,4-, 1,5-, and 2,6-Dialkoxyanthraquinones and 1,5-bis(2-oligo(ethyleneoxy))anthraquinones (EO_nAQ, $n = 1-3$) derivatives were used as anthraquinone comonomers in the current study. This paper presents the results of the model compound studies and condensation polymerization of 1,4-, 1,5-, and 2,6-disubstituted anthraquinones with PDA and SDA.

Much information about the chemistry and the structure of a polymer can be obtained from a study of model compounds. We have previously reported the synthesis and characterization of the model compound for the simplest poly(anthraquinone diimine), namely *N*,*N*′-diphenylanthraquinone 9,10-diimine (DAQ).[7,8] The X-ray crystallographic analysis indicated that a *syn* diimine configuration was preferred in the solid state, but solution ^{1}H NMR indicated that this particular diimine exists in both the *syn* and *anti* configurations in dynamic equilibrium. To obtain polymers that would exist in only a single diimine configuration, disubstituted anthraquinones were chosen as likely candidates. In a recent paper we reported the first disubstituted anthraquinone diimine model compounds, *N*,*N*′-diphenyl-1,5-dimethoxyanthraquinone 9,10-diimine (15DMAQ) and *N*,*N*′-diphenyl-1,4-dimethoxyanthraquinone 9,10-diimine (14DMAQ), shown in Figure 1.[9] It was shown by ^{1}H NMR spectroscopy and X-ray crystal structure analysis that the methoxy substituent was within the *N*-phenyl ring's shielding region in all cases, thus giving

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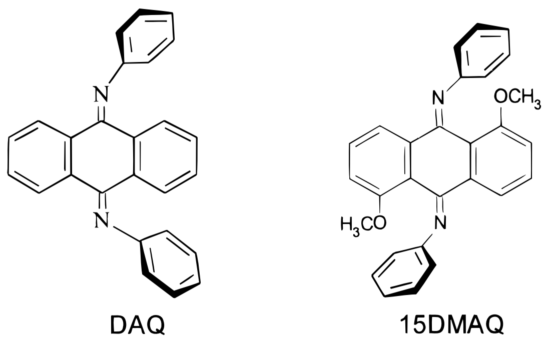


DAQ 15DMAQ

Figure 1. Model compounds N,N'-diphenylanthraquinone 9,10-diimine (DAQ), N,N'-diphenyl-1,5-dimethoxyanthraquinone 9,10-diimine (15DMAQ) with corresponding configuration as confirmed by X-ray crystallographic analysis.

rise to an *anti* configuration for 15DMAQ and a *syn* configuration for 14DMAQ. Using variable temperature NMR, we had determined that DAQ isomerizes with an energy barrier of 17.5 kcal/mol.[10] In contrast, 15DMAQ did not isomerize to the syn isomer in a variable temperature NMR experiment up to 180 °C, indicating that the imine functionality is rigid and locked in the anti configuration in the methoxy-substituted model compound. All anthraquinone diimines with substituents in the *peri*-positions were locked in either the *syn* or the *anti* configuration.

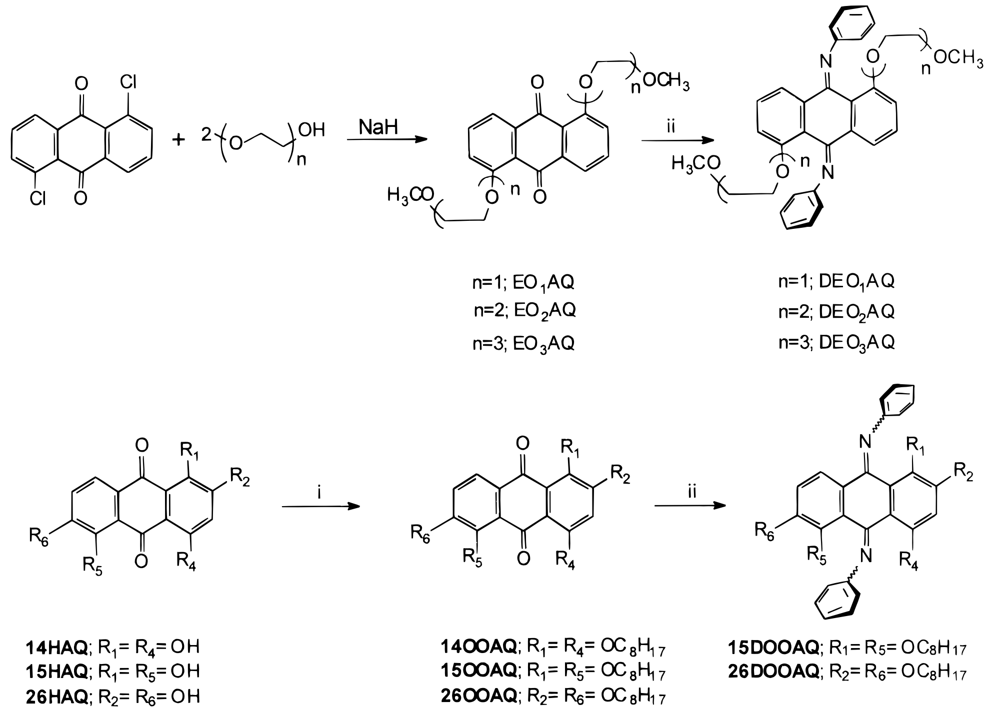
The N,N'-diphenylanthraquinone 9,10-diimines are not planar but buckled into a butterfly configuration. In solution, anthraquinone diimines rapidly invert between the two possible butterfly configurations. The energy barrier for the "butterfly" inversion of *peri*-substituted anthraquinone diimines is raised because of the increased steric bulk of the methoxy substituent compared to the *peri*-hydrogen of the unsubstituted DAQ, further increasing the rigidity of the dimethoxy-substituted N,N'-diphenyl diimines.[7] The rigid dimethoxy-substituted N,N'-diphenyl diimines were less soluble than the parent DAQ, and therefore we decided to investigate anthraquinone derivatives with other solubilizing substituents.

Results and Discussion

Model Compounds. Anthraquinones with longer side chains were desired to impart greater solubility to these more structurally rigid diimines.[11] Two varieties of alkoxy-substituted anthraquinones were easily synthesized using slight modifications of literature procedures. The synthesis of the symmetrically substituted anthraquinones are illustrated in Scheme 1. Symmetrically disubstituted ethyleneoxy derivatives were synthesized in one step by nucleophilic aromatic substitution of 1,5-dichloroanthraquinone with oligo(ethyleneoxy) alcohols under alkaline conditions.[12-14] The 1,5-bis(2-oligo(ethyleneoxy))anthraquinones with (EO$_n$AQ, $n = 1-3$) were completely soluble in common organic solvents and became slightly water soluble as the side chain length increased. 1,4-, 1,5-, and 2,6-Dialkoxyanthraquinones (14-, 15-, and 26OOAQ) were synthesized by slight modifications of a method described by Preston and co-workers.[15] 1,4-, 1,5-, and 2,6-Dihydroxyanthraquinones were alkylated using 1-iodooctane with KF on Al_2O_3 (40% w/w) as a base in acceptable yields. 2,6-Bis(octyloxy)anthraquinone was the least soluble of the alkoxy series but still exhibited excellent solubility compared to AQ itself in common organic solvents.

Model compounds were synthesized by condensing 2 equiv of aniline and EQ$_n$AQ, $n = 1-3$, 15OOAQ and 26OOAQ in the presence of $TiCl_4$ and DABCO to give the N,N'-diphenyl-1,5-bis(2-methoxyethoxy)anthraquinone 9,10-diimine (DEO$_1$AQ), N,N'-diphenyl-1,5-bis(2-(2-methoxyethoxy)ethoxy)anthraquinone 9,10-diimine (DEO$_2$AQ), N,N'-diphenyl-1,5-bis(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)anthraquinone 9,10-diimine (DEO$_3$AQ), N,N'-diphenyl-1,5-bis(octyloxy)anthraquinone 9,10-diimine (15DOOAQ), and N,N'-diphenyl-2,6-bis(octyloxy)-

Scheme 1. Synthesis of (A) N,N'-Diphenyl-1,5-bis(oligoethyleneoxy)anthraquinone 9,10-diimine (DEO$_n$AQ, $n = 1-3$) and (B) N,N'-Diphenyl bis(octyloxy)anthraquinone 9,10-diimine



n=1; EO$_1$AQ
n=2; EO$_2$AQ
n=3; EO$_3$AQ

n=1; DEO$_1$AQ
n=2; DEO$_2$AQ
n=3; DEO$_3$AQ

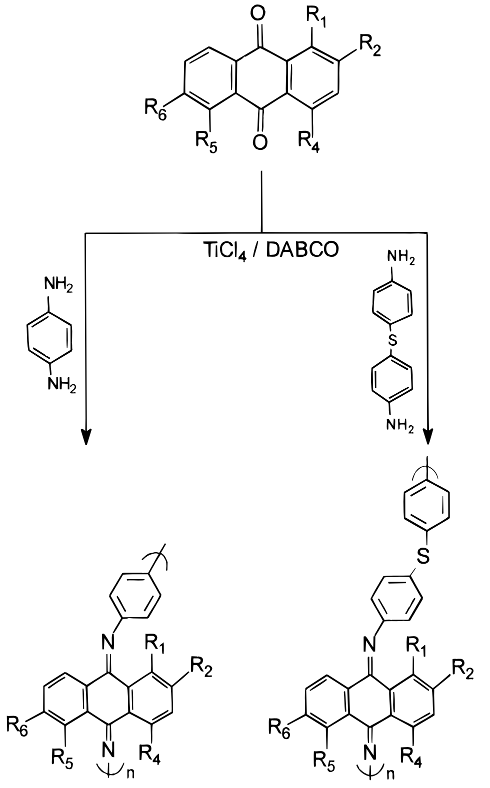
14HAQ; $R_1 = R_4 = OH$
15HAQ; $R_1 = R_5 = OH$
26HAQ; $R_2 = R_6 = OH$

14OOAQ; $R_1 = R_4 = OC_8H_{17}$
15OOAQ; $R_1 = R_5 = OC_8H_{17}$
26OOAQ; $R_2 = R_6 = OC_8H_{17}$

15DOOAQ; $R_1 = R_5 = OC_8H_{17}$
26DOOAQ; $R_2 = R_6 = OC_8H_{17}$

i.) KF/ AL_2O_3, $C_8H_{17}I$ ii.) $TiCl_4$, DABCO, 2 equiv. Aniline

Scheme 2. Polymerization of Symmetrically Disubstituted Anthraquinones with SDA and PDA



$R_1=R_5=(OCH_2CH_2)_nOCH_3$, $R_2=R_4=R_6=H$; **EO$_n$AQ n=1- 3**
$R_1=R_4=OC_8H_{17}$, $R_2=R_5=R_6=H$; **14OOAQ**
$R_1=R_5=OC_8H_{17}$, $R_2=R_4=R_6=H$; **15OOAQ**
$R_2=R_6=OC_8H_{17}$, $R_1=R_4=R_5=H$; **26OOAQ**

anthraquinone 9,10-diimine (26DOOAQ) model compounds, respectively, as shown in Scheme 2. The *N*,*N*′-diphenyl diimine model compounds were isolated as yellow crystalline solids, except for DEO$_3$AQ which was a semiwaxy liquid at ambient temperatures.

The *N*,*N*′-diphenyl diimine model compounds were characterized by ^{1}H NMR spectroscopy. In the DEO$_n$AQ, $n = 1-3$, series, the *anti* configuration observed for 15DMAQ was confirmed by ^{1}H NMR spectroscopy by a large upfield shift for the methylene resonances of the ethyleneoxy substituents and the symmetrical pattern in the aromatic spectral region. The upfield shift for the methylene resonances of the ethyleneoxy substituents indicates these substituents are within the *N*-phenyl ring's shielding region giving the expected *anti* configuration. The *anti* diimine configuration is attributed to repulsive interactions between the lone pair of electrons on the nitrogen atom and the lone pair of electrons on the oxygen atom similar to that experienced in the *N*,*N*′-diphenyl diimine 15DMAQ.[7]

The dioctyloxy-substituted *N*,*N*′-diphenyl diimine model compound 15DOOAQ also existed in the *anti* configuration, as expected. The *anti* configuration was confirmed by ^{1}H NMR spectroscopy, which revealed an upfield shift for the first two methylene units attached closest to the AQ ring and a symmetrical aromatic spectral region. In contrast, 26DOOAQ showed no preference for either a *syn* or *anti* configuration. The latter's ^{1}H NMR spectrum was complicated and asymmetrical in the aromatic region, giving multiplets for the AQ ring hydrogens. In addition, the methylene units closest to the AQ ring system gave multiple peaks in the methoxy region. These data are consistent with our hypothesis that both *syn* and *anti* configurations are present in solution, similar to the case with DAQ. The alkoxy substituents are too far removed from the imine functionality to experience the electronic repulsion of the nitrogen lone pairs; thus no configurational control can be obtained using 26OOAQ as a comonomer.

Table 1. Molecular Weights of Poly(quinone imines)

		SEC data		
quinone monomer	diamine monomer	% high MW of reacn mixture	M_w high MW fractions	M_n high MW fractions
EOAQ	SDA	70.1	15 800	8400
EOAQ	PDA	60.1	2 100	2000
EO$_2$AQ	SDA	91.9	30 800	21900
EO$_2$AQ	PDA	64.1	14 100	3600
EO$_3$AQ	SDA	82.4	34 200	25300
EO$_3$AQ	PDA	60.3	3 500	3300
14OOAQ	SDA	55.4	16 300	14400
14OOAQ	PDA	86.0	5 000	2200
15OOAQ	SDA	84.4	27 100	21700
15OOAQ	PDA	70.2	7 800	5400
26OOAQ	SDA	36.5	32 700	26800
26OOAQ	PDA	74.3	23 300	5900

The UV–vis spectra of the *N*,*N*′-diphenyl diimine model compounds exhibit absorption maxima at 368–398 nm. The extinction coefficients of the model compounds are large $\sim 10 \times 10^4$ M^{-1} cm^{-1}. *N*,*N*′-Diphenyl diimine model compounds synthesized from anthraquinones symmetrically disubstituted in the *peri*-positions with sterically bulky alkoxy substituents have a larger buckling of the central ring system.[5,7] The larger buckling of the central ring system further decreases the amount of extended conjugation, hence lower absorption maxima for these molecules. When AQ is substituted in the 2,6-position, the steric interactions are minimized and the *N*,*N*′-diphenyl diimine buckling should return to the normal 26°, as indicated by a λ_{max} of 398 nm obtained for 26DOOAQ, similar to that of DAQ (λ_{max} of 398 nm). Therefore we can conclude that, in spite of the apparent conjugation on paper, the *N*,*N*′-diphenyl anthraquinone diimines are not in formal conjugation owing to the lack of planarity.

Polymerizations. Model compound studies suggested that stereoregular polymers could be obtained with either a *syn* or *anti* configuration depending upon the substitution pattern of the AQ. Generating polymers with precisely controlled structures could theoretically permit fine tuning and enhancement of the polymers opto-electronic properties. The poly(quinone imines) obtained from disubstituted anthraquinone and aromatic diamines were expected to be stereoregular, have high molecular weights, and have increased solubility permitting ease in characterization and processing.

Relative molecular weights were determined by SEC in THF and are summarized in Table 1. The polymerizations with the longer side chained anthraquinones were carried out using the TiCl$_4$/DABCO polycondensation conditions, as illustrated in Scheme 2.

The polymerization of 1,5-dimethoxyanthraquinone (15MAQ) with SDA using the established imine polycondensation conditions gave poor yields of oligomers (M_w = 1300). Soxhlet extraction of the titanium/DABCO salts for 72 h with chlorobenzene gave less than 10% yields of the oligomeric material. The isolated oligomers were sparingly soluble in THF, CHCl$_3$, and hot chlorobenzene, making characterization difficult. Model compound studies of dimethoxy-substituted anthraquinone diimines suggested that polymers would exist primarily in a single configuration depending upon the substitution pattern, significantly decreasing the molecular motion of the substituted poly(quinone diimines) compared to the parent poly(quinone diimine). The decreased solubility of the SDA/15MAQ polymer can be attributed to the decreased molecular motion ascribed to the all-*anti* configuration and the raised energy barrier for the butterfly inversion. 1,4-Dimethoxyanthraquinone (14MAQ) was polymerized with PDA to give an intractable product in low yields, similar to the results obtained with 15MAQ. No high molecular weight polymer was formed, and the isolated product was insoluble and difficult to characterize. The low yields and insolubility of the PDA/14MAQ polycondensation can be attributed to the same reasons mentioned for the 15MAQ/SDA system.

The anthraquinones possessing longer side chains gave better results. The longer solubilizing side chains overcame the solubility barriers of a single configuration and the limited motion of the butterfly inversion, keeping the polymers in solution and allowing growth to higher molecular weights.

EO_1AQ was polymerized with both SDA and PDA. SEC analysis of the polymers prepared from EO_1AQ revealed that SDA polymerizations gave polymers with molecular weights of M_w 15 800 in moderate yields (70%). The remaining fraction was a series of resolved low molecular weight components. These distinct low molecular weight components have been previously identified by fast atom bombardment mass spectrometry (FAB-MS) analysis and IR end group analysis to be macrocyclic imines that are formed as byproducts of the polymerization.[4] The presence of macrocycles in the all-*trans* configuration of an EO_1AQ/SDA system gives an indication of the propensity of imines to form macrocycles. No attempts were made to maximize macrocycle formation. Use of the less soluble diamine PDA as comonomer gave oligomers (M_w 2100) in moderate yields (59%). We propose that the intractibility of the material caused the yields to be lower for the EO_1AQ polycondensations. These results suggest that an $n = 1$ side chain is not able to overcome the solubility barrier with PDA, but is able to overcome the solubility problems when the more soluble SDA is used as the comonomer.

SEC analysis of EO_2AQ polycondensations revealed mostly high molecular weight polymer for both SDA (M_w 30 800) and PDA (M_w 14 000) aromatic diamines. The remaining fraction (8.1%) of material in SDA polymerizations was again a series of distinct low molecular weight macrocycles as determined by SEC and IR end group analysis. The poly(quinone imines) of EO_2AQ were soluble in THF and chlorobenzene and could be cast into thin films. Therefore an $n = 2$ side chain is able to overcome the solubility problems with both the SDA and PDA diamine comonomers.

EO_3AQ was polymerized with SDA to give mostly polymer having molecular weights of M_w 34 000, M_n 25 300 with the remaining fraction (18.6%) consisting of macrocycles as determined by SEC and IR analysis. Polymerizations incorporating PDA with EO_3AQ presented an unexpected obstacle. Polymerizations incorporating PDA as a comonomer require refluxing *o*-dichlorobenzene (bp 179 °C) as the reaction solvent. These high-temperature conditions resulted in significant decomposition of the quinone. A black, mostly insoluble product was isolated. IR confirmed the presence of the imine functionality, suggesting that the EO_3AQ decomposed because of the elevated reaction temperatures and not by a nucleophilic attack of the titanium amine complex on the ethyleneoxy side chain. EO_3AQ was heated to 100 °C without any solvent present for 12 h. The quinoid compound melted into a bright yellow liquid and then slowly decomposed to a brown liquid. EO_3AQ therefore is not suitable for polycondensations at high temperatures. The polymerization was repeated in chlorobenzene (bp 131 °C) and only low molecular weight polymer (M_w 3500) was obtained at these lowered temperatures. A waxy polymer was obtained which was red in color and soluble in common organic solvents. ^{1}H NMR characterization of the polymers incorporating 1,5-disubstituted EO_nAQ, $n = 1-3$, with SDA and PDA confirmed the *anti* configuration of the poly(quinone imines).

Polymerizations were also carried out using octyloxy-substituted anthraquinones with SDA and PDA as comonomers, as shown in Scheme 2. The substitution pattern of the AQ chosen controls the configuration of the resultant polymer. On the basis of model compound results, we expect that 1,4- and 1,5-disubstituted anthraquinones will result in all *syn* and all *anti* configurations, respectively. A 2,6-disubstituted AQ will not give stereoregular polymers, as model compound studies have indicated, but will increase the polymers solubility, making processing of the final polymer easier.

Polymerizations of octyloxyanthraquinones with SDA gave mostly high molecular weight M_w 30 000, M_n 21 000 red amorphous polymers. The remaining distinct low molecular weight fraction was a series of macrocycles, as determined by SEC and IR end group analysis. Polymers were obtained with an all *anti* configuration with 15OOAQ and an all *syn* configuration for the 14OOAQ, as confirmed by ^{1}H NMR spectroscopy. An asymmetric aromatic region and multiple peaks for the methylene resonance indicated that no stereoregular polymer was obtained with 26OOAQ. Polymers incorporating these disubstituted anthraquinones have the same relative configuration as the *N*,*N'*-diphenyl model compounds. 14OOAQ/SDA polymers are of lower relative molecular weight with a larger fraction (44.4%) of the sample being macrocycles when compared to the other substituted AQ/SDA systems. These data indicate that the rigid *syn* diimine configuration makes macrocyclic imine formation much more likely than in the rigid *anti* or isomerizable diimine configurations. No macrocycles could be detected in polymerizations incorporating PDA.

Polymerizations of PDA with 14OOAQ and 15OOAQ yielded red polymers with molecular weights ~8000 which were stereoregular, as determined by ^{1}H NMR. Polymerizations incorporating PDA with 26OOAQ gave amorphous polymers with molecular weights of M_w 23 000, M_n 5 900 which were red in color. The polymerizations incorporating 26OOAQ yielded polymers with no stereoregularity, but these polymers do have increased solubility. ^{1}H NMR spectroscopic analysis of the polymers revealed an asymmetric aromatic region and multiple peaks for the methylene unit closest to the quinone ring system, similar to the observations above with SDA and 26OOAQ polymerizations.

The PDA polymerizations of 14OOAQ and 15OOAQ are inhibited by steric hindrance of the side chains, limiting the polymer's growth. In some polymer configurations the bulky side chains on adjacent repeat units of 1,4- and 1,5-disubstituted anthraquinones will interact with each other as they attempt to occupy the

Table 2. Ultraviolet Data for Model Compounds and Polymers of Substituted Anthraquinones in Tetrahydrofuran

quinone	λ_{max} for model compd (nm)	λ_{max} for SDA polymer (nm)	λ_{max} for PDA polymer (nm)
AQ[a]	398	424	468
15MAQ	368[b]	410	
14MAQ	372[b]		430
EOAQ	374[b]	414	440
EO_2AQ	370[b]	424	447
EO_3AQ	372[b]	412	460[b]
15OOAQ	372	424	446
26OOAQ	398	424	472
14OOAQ		398	428

[a] See ref 4 for experimental details. [b] UV–vis data were recorded in $CHCl_3$.

same space within the *N*-phenyl ring's shielding region. The preferred anti-configuration of the alkoxy side chains will increase the likelihood of steric interactions between adjacent repeat units resulting in lower molecular weights. The steric interactions of EO_nAQ, $n = 1-3$, anthraquinone side chains are less than alkoxy side chains due to the preferred gauche conformation of the ethyleneoxy substituents,[16] as evidenced by a successful polymerization of EO_2AQ and PDA. The undesirable steric interactions were avoided in polymerizations incorporating SDA and peri-substituted anthraquinones due to the additional phenyl spacer linkage of SDA. SDA polymerizations resulted in higher molecular weight polymers for all of the anthraquinones investigated.

The UV–vis spectra of the substituted polyquinone imines exhibit absorption maxima at 410–472 nm, which are shifted to longer wavelengths than the corresponding *N,N′*-diphenyl diimine model compounds (Table 2). The extinction coefficients of the polymers and model compounds are on the same order of magnitude, namely 10×10^4 M^{-1} cm^{-1}. The polymers containing *peri*-substituted anthraquinones and SDA generally absorbed at wavelengths by 10 nm shorter than 26OOAQ/SDA and the parent AQ/SDA poly(quinone imines). These data indicate less extended conjugation due to the larger buckling of the central ring system.[17] Polymers containing *peri*-substituted anthraquinones and PDA are shifted to shorter wavelengths than the 26OOAQ/PDA and parent AQ/PDA poly(quinone imines) by 15–25 nm. The all *syn* 14DOOAQ/PDA and 14DOOAQ/SDA polymers are shifted by 40 and 25 nm to shorter wavelengths, respectively, compared to the unsubstituted corresponding poly(quinone imines). The lower λ_{max} indicates that the *syn* configuration of these polymers is less conjugated than the *anti* polymers. The highest λ_{max} values were obtained for the more conjugated and less buckled 26OOAQ/PDA polymer system (472 nm). All polymers containing SDA and EO_nAQ, $n = 1-3$, were yellow in color and all polymers incorporating PDA were red in color after precipitation from hexanes. The observed color is an indication of reduced conjugation length in the SDA polymers compared to the more conjugated PDA polymers. The difference in color between the model compounds and the PDA-containing polymers may also be due to the increased conjugation length in the polymer chains.

No T_g values of the polymers could be obtained by DSC. The poly(quinone imines) decomposed before undergoing a glass transition. The poly(quinone imines) incorporating SDA were thermally stable only to 150 °C. Poly(quinone imines) incorporating PDA were thermally stable up to 175 °C. The polymers formed brittle thin films which were not suitable for mechanical testing. The poly(quinone imines) as synthesized are in the fully oxidized oxidation level. In order to obtain the emeraldine base analogs, the polymers will have to be selectively reduced.[18] The reduction studies are in progress and will be published elsewhere.

Conclusion

Poly(anthraquinone imines) with a strictly all *anti* configuration or all *syn* configuration were obtained from 1,5- and 1,4-disubstituted anthraquinones, respectively, with both SDA and PDA. Polymerizations incorporating SDA gave polymers with significant molecular weights for both the EO_nAQ, $n = 1-3$, anthraquinone and octyloxyanthraquinone series. Polymerizations incorporating PDA gave polymers with significant molecular weights for only the EO_nAQ, $n = 2$, and 26OOAQ anthraquinones. Limitations for successful polymerization results are attributed to solubility problems of the all *anti* configuration, steric hindrance of side chains on successive repeat units with *peri*-substituents, and decomposition of the EO_3AQ comonomer.

Experimental Section

General Considerations. NMR spectra were recorded on a Varian Unity 300 NMR spectrometer at 300 MHz. IR spectra were obtained on a Nicolet Impact 400D FT infrared spectrophotometer with OMNIC acquisition software. UV–visible spectra were obtained on a Hewlett Packard 8452A diode array spectrophotometer. Melting points were obtained on a Thomas-Hoover melting point apparatus and are corrected. Elemental analyses were performed by Desert Analytics, Tucson, AZ. Mass spectra were obtained by direct insertion probe at the University of Arizona Department of Chemistry mass spectrometry facility on a Hewlett-Packard 5988A with an RTE-6 data system at a source temperature of 200 °C. Molecular weights were determined by size exclusion chromatography using a Beckman 160 UV detector and Phenomenex Phenogel columns (10^5, 10^4, and 10^3 Å or 10^3, 500, 100 Å) in THF at ambient temperature. Molecular weight calculations were based on polystyrene standards.

Chemical Purification. The solvents chlorobenzene and *o*-dichlorobenzene were dried and distilled over P_2O_5 prior to use. THF was dried and distilled over sodium metal prior to use. *p*-Phenylenediamine (PDA) was sublimed prior to use. 4,4′-Thiodianiline (SDA) was vacuum distilled in a Kugelrohr apparatus at 200 °C/0.35 Torr. 1,4-Diazabicyclo[2.2.2]octane DABCO was dried by azeotropic distillation of water with benzene. The benzene was removed *in vacuo* followed by recrystallization of the product from anhydrous ether. Aniline was dried over potassium hydroxide and vacuum distilled (68 °C/0.10 Torr) prior to use. All other reagents were used as received from Aldrich.

Anthraquinones. The synthesis and characterization of 1,5-dimethoxyanthraquinone (15MAQ) and 1,4-dimethoxyanthraquinone (14MAQ) were reported previously.[7,19,20]

1,5-Bis(2-methoxyethoxy)anthraquinone (EOAQ). 2-Methoxyethanol (9.9 mmol, 0.75 g) was added dropwise to a stirred slurry of sodium hydride (9.9 mmol, 0.23 g) in 25 mL of THF, and the mixture was heated in an oil bath at 65 °C for 45 min. 1,5-Dichloroanthraquinone (4.12 mmol, 1.14 g) was added all at once. Then the mixture was stirred for 12 h. The reaction mixture was cooled, and the THF was removed *in vacuo*. The resulting solids were then redissolved in 75 mL of methylene chloride and washed with 2 × 100 mL of water and dried over $MgSO_4$. The crude product was obtained by removing methylene chloride *in vacuo*. Recrystallization from ethyl acetate gave the product as a bright yellow solid. Yield, %: 62.0. Mp: 146–147 °C. ^{1}H-NMR, δ ($CDCl_3$, 25 °C): 3.53

(s, 6H), 3.91 (t, 4H), 4.30 (t, 4H), 7.28 (d, 2H), 7.66 (t, 2H), 7.91 (d, 2H). ^{13}C-NMR, δ (CDCl$_3$, 25 °C): 197.7, 182.1, 158.9, 137.2, 134.6, 121.2, 119.9, 118.4, 70.7, 69.1, 59.3. IR (KBr): 2992, 1661 (C=O), 1584, 1466, 1262, 1022, 768 cm^{-1}. Mass spec, *m*/*z*: (M$^+$) 356, 324, 253, 59 (100), 29. UV−vis: $\lambda_{\max}$ (THF) 377 nm, ϵ = 3200 M^{-1} cm^{-1}. Anal. Calcd for $C_{20}H_{20}O_6$: C, 67.41; H, 5.67. Found: C, 67.18; H, 5.67.

1,5-Bis(2-(2-methoxyethoxy)ethoxy)anthraquinone (EO$_2$AQ). The same procedure as for DEOAQ was used, except 2-(2-methoxyethoxy)ethanol was used as the nucleophilic agent. Yield, %: 71.3 (yellow solid). Mp: 84−85 °C. ^{1}H-NMR, δ (CDCl$_3$, 25 °C): 3.39 (s, 6H), 3.59 (t, 4H), 3.84 (t, 4H), 4.02 (t, 4H), 4.32 (t, 4H), 7.28 (d, 2H), 7.66 (t, 2H), 7.90 (d, 2H). ^{13}C-NMR, δ (CDCl$_3$, 25 °C): 197.7, 182.1, 158.9, 137.2, 134.6, 121.2, 119.8, 118.4, 71.8, 70.9, 69.3, 58.9. IR (KBr): 2935, 1670 (C=O), 1586, 1455, 1287, 1023, 765 cm^{-1}. Mass spec, *m*/*z*: (M$^+$) 444, 253, 238, 59 (100), 45. UV−vis: $\lambda_{\max}$ (THF) 378 nm, ϵ = 9500 M^{-1} cm^{-1}. Anal. Calcd for $C_{24}H_{28}O_8$: C, 64.84; H, 6.30. Found: C, 64.64; H, 6.25.

1,5-Bis(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)anthraquinone (EO$_3$AQ). The same procedure as for DEOAQ was used, except 2-(2-(2-methoxyethoxy)ethoxy)ethanol was used as the nucleophilic agent. Yield, %: 60.4 (yellow solid). Mp: 46−49 °C. ^{1}H-NMR, δ (CDCl$_3$, 25 °C): 3.37 (s, 6H), 3.55 (t, 4H), 3.64 (t, 4H), 3.70 (t, 4H), 3.85 (t, 4H), 4.04 (t, 4H), 4.32 (t, 4H), 7.28 (d, 2H), 7.66 (t, 2H), 7.85 (d, 2H). ^{13}C-NMR, δ (CDCl$_3$, 25 °C): 197.6, 181.8, 158.7, 137.5, 120.9, 119.6, 118.3, 71.6, 70.8, 70.4, 70.2, 69.2, 69.1, 58.7. IR (KBr): 2881, 1664 (C=O), 1583, 1449, 1274, 1007, 764 cm^{-1}. Mass spec, *m*/*z*: (M$^+$) 532, 456, 267, 59 (100), 29. UV−vis: $\lambda_{\max}$ (THF) 379 nm, ϵ = 7300 M^{-1} cm^{-1}. Anal. Calcd for $C_{28}H_{36}O_{10}$: C, 63.17; H, 6.76. Found: C, 63.46; H, 6.66.

1,5-Bis(octyloxy)anthraquinone (15OOAQ). Octyl iodide (103.2 mmol, 24.8 g) was added dropwise to a stirred mixture of 1,5-dihydroxyanthraquinone (25.8 mmol, 6.19 g) and potassium fluoride on alumina (40%, 0.512 mol, 74.24 g) in DMSO at 85 °C for 10 h.[21] The reaction mixture was then filtered and extracted with 200 mL of CHCl$_3$, then washed with 5 × 100 mL of basic water and followed by 2 × 50 mL of neutral water and dried over MgSO$_4$. The solvent was removed *in vacuo*, giving the crude product. Repeated recrystallization from hexanes gave the product as a bright yellow crystalline solid. Yield, %: 56.8. Mp: 89−91 °C. ^{1}H-NMR, δ (CDCl$_3$, 25 °C): 0.88 (t, 6H), 1.34 (m, 16H), 1.56 (p, 4H), 1.96 (p, 4H), 4.15 (t, 4H), 7.22 (d, 2H), 7.66 (t, 2H), 7.89 (d, 2H). ^{13}C-NMR, δ (CDCl$_3$, 25 °C): 14.1, 22.6, 25.9, 29.1, 29.5, 31.8, 69.6, 112.6, 119.5, 134.8, 137.5, 159.3, 182.5, 197.8. IR (KBr): 2922, 1665 (C=O), 1590, 1380, 1274, 952, 725 cm^{-1}. Mass spec, *m*/*z*: (M$^+$) 464, 365, 267, 240, 224, 69, 43 (100). UV−vis: $\lambda_{\max}$ (THF) 378 nm, ϵ = 6600 M^{-1} cm^{-1}. Anal. Calcd for $C_{30}H_{40}O_4$: C, 77.55; H, 8.68. Found: 77.56; H, 8.67.

1,4-Bis(octyloxy)anthraquinone (14OOAQ). The same procedure as for 15OOAQ was used, but substituting 1,4-dihydroxyanthraquinone for 1,5-dihydroxyanthraquinone. Yield, %: 47.4 (yellow crystals). Mp: 80−81 °C. ^{1}H-NMR, δ (CDCl$_3$, 25 °C): 0.90 (t, 6H), 1.29 (m, 12H), 1.35 (p, 4H), 1.56 (p, 4H), 1.92 (p, 4H), 4.09 (t, 4H), 7.30 (s, 2H), 7.68 (dd, 2H), 8.16 (dd, 2H). ^{13}C-NMR, δ (CDCl$_3$, 25 °C): 12.5, 23.0, 25.5, 30, 32.2, 71, 122.5, 127, 133.5, 154, 197.8. IR (KBr): 2922, 1665 (C=O), 1592, 1380, 1274, 952, 723 cm^{-1}. Mass spec, *m*/*z*: (M$^+$) 464, 365, 267, 240, 211, 128, 43 (100). UV−vis: $\lambda_{\max}$ (THF) 410 nm, ϵ = 6500 M^{-1} cm^{-1}. Anal. Calcd for $C_{30}H_{40}O_4$: C, 77.55; H, 8.68. Found: C, 77.72; H, 8.64.

2,6-Bis(octyloxy)anthraquinone (26OOAQ). The same procedure as for 15OOAQ was used, but substituting 2,6-dihydroxyanthraquinone for 1,5-dihydroxyanthraquinone. Yield, %: 56.3 (dull yellow crystals). Mp: 105−106 °C. ^{1}H-NMR, δ (CDCl$_3$, 25 °C): 0.90 (t, 6H), 1.33 (m, 16H), 1.46 (p, 4H), 1.84 (p, 4H), 4.14 (t, 4H), 7.20 (dd, 2H), 7.70 (s, 2H), 8.21 (d, 2H). ^{13}C-NMR, δ (CDCl$_3$, 25 °C): 14.0, 22.6, 25.9, 29.0, 29.3, 31.8, 68.7, 110, 112.9, 120.8, 126.9, 129.5, 135.7, 163.9, 182.1, 197.8. IR (KBr): 2927, 2851, 1661 (C=O), 1586, 1375, 1299, 1080, 742 cm^{-1}. Mass spec, *m*/*z*: (M$^+$) 464, 352, 240 (100), 212, 71, 43. UV−vis: $\lambda_{\max}$ (THF) 346 nm, ϵ = 15 200 M^{-1} cm^{-1}. Anal. Calcd for $C_{30}H_{40}O_4$: C, 77.55; H, 8.68. Found: C, 77.18; H, 8.49.

Model Compounds. The synthesis and characterization of *N*,*N*′-diphenyl-1,5-dimethoxyanthraquinone 9,10-diimine (15DMAQ) and *N*,*N*′-diphenyl-1,4-dimethoxyanthraquinone 9,10-diimine (14DMAQ) were reported previously.[7]

***N*,*N*′-Diphenyl-1,5-bis(2-methoxyethoxy)anthraquinone 9,10-Diimine (DEOAQ).** Aniline (2.4 mmol, 0.20 g) and DABCO (7.2 mmol, 0.81 g) were dissolved in 6 mL of chlorobenzene at 90 °C. Titanium tetrachloride (1.8 mmol, 0.34 g) in 3 mL of chlorobenzene was added dropwise over 15 min. The addition funnel was rinsed with 3 mL of chlorobenzene. EOAQ (1.2 mmol, 0.43 g) was added all at once via a powder addition funnel; the funnel was then rinsed with 2 mL of chlorobenzene. The reaction mixture was heated in an oil bath at 125 °C for 24 h. The product was isolated as a yellow solid by filtering off the precipitate and removing the solvent *in vacuo*. Yield, %: 93.4. Mp: 158−159 °C. ^{1}H-NMR, δ (CDCl$_3$, 25 °C): 3.27 (t, 8H), 3.32 (s, 6H), 6.75 (d, 2H), 6.91 (d, 4H), 7.06 (t, 2H), 7.20 (t, 4H), 7.45 (t, 2H), 7.81 (d, 2H). ^{13}C-NMR, δ (CDCl$_3$, 25 °C): 59.0, 67.1, 70.4, 112.6, 118.6, 120.5, 120.7, 124.4, 128.4, 131.5, 142.0, 151.0, 153.9, 156.2. IR (KBr): 3090, 2925, 1620 (C=N), 1583, 1466, 1232, 1122, 772, 695 cm^{-1}. Mass spec, *m*/*z*: (M$^+$) 506, 414, 390, 324 (100), 77, 59. UV−vis: $\lambda_{\max}$ (CHCl$_3$) 374 nm, ϵ = 9800 M^{-1} cm^{-1}. Anal. Calcd for $C_{32}H_{30}N_2O_4$: C, 75.95; H, 5.99; N, 5.53. Found: C, 75.60; H, 5.77; N, 5.37.

***N*,*N*′-Diphenyl-1,5-bis(2-(2-methoxyethoxy)ethoxy)anthraquinone 9,10-Diimine (DEO$_2$AQ).** The same procedure as for DEOAQ was used, but substituting 1,5-bis(2-methoxyethoxy)anthraquinone (EO$_2$AQ) for EOAQ. Yield, %: 92.9 (yellow solid). Mp: 88−92 °C. ^{1}H-NMR, δ (CDCl$_3$, 25 °C): 3.33 (t, 8H), 3.36 (s, 6H), 3.50 (m, 4H), 3.54 (m, 4H), 6.75 (d, 2H), 6.91 (d, 4H), 7.06 (t, 2H), 7.22 (t, 4H), 7.45 (t, 2H), 7.75 (d, 2H). ^{13}C-NMR, δ (CDCl$_3$, 25 °C): 59.0, 67.1, 69.0, 70.6, 71.9, 112.5, 118.3, 119.6, 120.7, 124.4, 128.3, 131.4, 142.0, 151.0, 153.9, 156.2. IR (KBr): 3051, 2874, 1621 (C=N), 1583, 1467, 1287, 1100, 790, 696 cm^{-1}. Mass spec, *m*/*z*: (M$^+$) 594, 426, 390, 324 (100), 77, 59. UV−vis: $\lambda_{\max}$ (CHCl$_3$) 370 nm, ϵ = 10 600 M^{-1} cm^{-1}. Anal. Calcd for $C_{36}H_{38}N_2O_6$: C, 72.71; H, 6.44; N, 4.71. Found: C, 72.43; H, 6.48; N, 4.67.

***N*,*N*′-Diphenyl-1,5-bis(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)anthraquinone 9,10-Diimine (DEO$_3$AQ).** The same procedure as for DEOAQ was used, but substituting 1,5-bis[2-(2-methoxyethoxy)ethoxy)]anthraquinone (EO$_3$AQ) for EOAQ. Yield, %: 86.5 (dark brown oil). ^{1}H-NMR, δ (CDCl$_3$, 25 °C): 3.30 (t, 8H), 3.35 (s, 6H), 3.52 (m, 8H), 3.54 (m, 8H), 6.75 (d, 2H), 6.91 (d, 4H), 7.06 (t, 2H), 7.20 (t, 4H), 7.45 (t, 2H), 7.85 (d, 2H). ^{13}C-NMR, δ (CDCl$_3$, 25 °C): 58.9, 67.1, 70.5, 70.6, 71.8, 118.3, 119.6, 120.6, 124.3, 128.3, 131.4, 142.0, 151.0, 153.9, 156.2. IR (KBr): 3051, 2875, 1619 (C=N), 1583, 1281, 1105, 772, 696 cm^{-1}. Mass spec, *m*/*z*: (M$^+$) 682, 590, 470, 390, 324 (100), 103, 59. UV−vis: $\lambda_{\max}$ (CHCl$_3$) 372 nm, ϵ = 8700 M^{-1} cm^{-1}. Anal. Calcd for $C_{40}H_{46}N_2O_8$: C, 70.36; H, 6.74; N, 4.10. Found: C, 70.68; H, 6.82; N, 4.15.

***N*,*N*′-Diphenyl-1,5-bis(octyloxy)anthraquinone 9,10-Diimine (15DOOAQ).** The same procedure as for DEOAQ was used, but substituting 1,5-dioctyloxyanthraquinone (15OOAQ) for EOAQ. Yield, %: 87.8 (yellow solid). Mp: 83−86 °C. ^{1}H-NMR, δ (CDCl$_3$, 25 °C): 0.93 (t, 6H), 1.34 (bs, 24H), 3.35 (b, 4H), 6.69 (d, 2H), 6.90 (d, 4H), 7.04 (t, 2H), 7.20 (t, 4H), 7.42 (t, 2H), 7.78 (d, 2H). ^{13}C-NMR, δ (CDCl$_3$, 25 °C): 14.5, 23.5, 26.1, 28.9, 29.6, 29.8, 32.3, 68.5, 112.5, 113.5, 118.2, 121.2, 124.7, 128.7, 131.8, 152. 153.9, 156.2. IR (KBr): 3051, 2874, 1621 (C=N), 1583, 1467, 1287, 1100, 790, 696 cm^{-1}. Mass spec, *m*/*z*: (M$^+$) 590, 522, 426, 390, 324, 77, 59, 43 (100). UV−vis: $\lambda_{\max}$ (THF) 372 nm, ϵ = 10 500 M^{-1} cm^{-1}. Anal. Calcd for $C_{42}H_{50}N_2O_2$: C, 82.04; H, 8.20; N, 4.56. Found: C, 81.82; H, 8.17; N, 4.55.

***N*,*N*′-Diphenyl-2,6-bis(octyloxy)anthraquinone 9,10-Diimine (26DOOAQ).** The same procedure as for DEOAQ was used, but substituting 2,6-dioctyloxyanthraquinone (26OOAQ) for EOAQ. Yield, %: 100 (waxy solid). ^{1}H-NMR, δ (CDCl$_3$, 25 °C): 0.80 (t, 6H), 1.19 (bs, 16H), 1.37 (p, 4H), 1.70 (p, 4H), 3.21 (dd, 2H), 3.99 (t, 2H), 4.09 (d, 2H), 6.39 (d, 1H), 6.54 (s, 1H), 6.74 (d, 1H), 6.82 (d, 4H), 7.00 (t, 2H), 7.14 (s, 1H), 7.24 (t, 4H), 7.58 (d, 1H), 7.71 (s, 1H), 8.12 (dd, 1H). ^{13}C-NMR, δ (CDCl$_3$, 25 °C): 13.6, 22.6, 25.9, 28.73, 29.19, 29.8, 31.75, 68.21, 110.5, 115.83, 116.45, 116.98, 119.81, 121.78, 122.53, 123.71, 129.08, 129.61, 130.15, 140.72, 151.59, 155.9, 160.4. IR (KBr): 3051, 2925, 1621 (C=N), 1589, 1467, 1280, 1105 cm^{-1}. Mass spec, *m*/*z*: (M$^+$) 614, 539, 389, 314, 240, 77, 43 (100). UV−vis: λ_{max} (THF) 398 nm, ϵ = 4700 M^{-1} cm^{-1}. Anal. Calcd for $C_{42}H_{50}N_2O_2$: C, 82.04; H, 8.20; N, 4.56. Found: C, 81.65; H, 8.03; N, 4.25.

Polymers. General Polymerization Procedure. 4,4′-Thiodianiline (1.2 mmol, 0.26 g) and DABCO (7.2 mmol, 0.81 g) were dissolved in 6 mL of chlorobenzene while heating at 90 °C. Titanium tetrachloride (1.8 mmol, 0.34 g) was added dropwise over 15 min. The addition funnel was rinsed with 3 mL of chlorobenzene. The anthraquinone (1.2 mmol) was added to the system all at once via a powder addition funnel. The funnel was then rinsed with 2 mL of chlorobenzene. The reaction mixture was heated in an oil bath at 125 °C for 24 h. The resulting polymer was isolated by filtering the precipitates. The filter cake was repeatedly washed with hot chlorobenzene until all polymer was removed, as indicated by a colorless filtrate stream. Chlorobenzene was removed *in vacuo* and the polymer was purified by dissolution in chloroform or THF and precipitation from hexanes. The polymerizations incorporating PDA were conducted in refluxing *o*-dichlorobenzene.

Polymerization of 1,5-Dimethoxyanthraquinone (15MAQ) and 4,4′-Thiodianiline. Yield, %: 5.52 (red solid). ^{1}H-NMR, δ (CDCl$_3$, 25 °C): 3.14 (s, 6H), 6.60 (d, 2H), 6.69 (d, 4H), 7.20 (b, 4H), 7.45 (t, 2H), 7.75 (d, 2H). IR (KBr): 3070, 2960, 1620 (C=N), 1578, 1260, 1125, 705 cm^{-1}. UV−vis: λ_{max} (THF) 410 nm, ϵ = 10 700 M^{-1} cm^{-1}.

Polymerization of 1,4-Dimethoxyanthraquinone (14MAQ) and *p*-Phenylenediamine. Yield, %: 24.4 (dark brown solid). ^{1}H-NMR, δ (CDCl$_3$, 25 °C): 3.14 (s, 6H), 6.60 (b, 4H), 7.50 (b, 2H), 8.1 (b, 2H), 8.5 (b, 2H). IR (KBr): 3070, 2960, 1615 (C=N), 1578, 1500, 1260, 1050, 805 cm^{-1}.

Polymerization of 1,5-Bis(2-methoxyethoxy)anthraquinone (EOAQ) and 4,4′-Thiodianiline. Yield, %: 54.7 (yellow solid). ^{1}H-NMR, δ (CDCl$_3$, 25 °C): 3.25 (s, 6H), 3.26 (m, 8H), 6.75 (b, 2H), 6.91 (b, 4H), 7.20 (b, 4H), 7.45 (b, 2H), 7.81 (d, 2H). IR (KBr): 3090, 2923, 1619 (C=N), 1572, 1260, 1125, 702 cm^{-1}. UV−vis: λ_{max} (THF) 414 nm, ϵ = 16 000 M^{-1} cm^{-1}. Anal. Calcd for $C_{32}H_{28}N_2O_{4S}$: C, 71.62; H, 5.26; N, 5.22; S, 5.97. Found: C, 70.15; H, 4.43; N, 4.96.

Polymerization of 1,5-Bis(2-methoxyethoxy)anthraquinone (EOAQ) and *p*-Phenylenediamine. Yield, %: 58.8 (red solid). ^{1}H-NMR, δ (CDCl$_3$, 25 °C): 3.20 (s, 6H), 3.30 (m, 8H), 6.75 (b, 2H), 6.91 (b, 4H), 7.20 (b, 4H), 7.55 (b, 2H), 7.81 (d, 2H). IR (KBr): 3090, 2913, 1619 (C=N), 1565, 1277, 1052, 837 cm^{-1}. UV−vis: λ_{max} (THF) 440 nm, ϵ = 7300 M^{-1} cm^{-1}. Anal. Calcd for $C_{26}H_{24}N_2O_4$: C, 72.88; H, 5.65; N, 6.54. Found: C, 70.75; H, 5.14; N, 5.10.

Polymerization of 1,5-Bis(2-(2-methoxyethoxy)ethoxy)anthraquinone (EO$_2$AQ) and 4,4′-Thiodianiline. Yield, %: 97.3 (bright yellow solid). ^{1}H-NMR, δ (CDCl$_3$, 25 °C): 3.11 (s, 6H), 3.35 (m, 8H), 3.50 (d, 4H), 3.85 (m, 4H), 6.75 (d, 2H), 6.80 (d, 4H), 7.18 (d, 4H), 7.45 (t, 2H), 7.79 (d, 2H). IR (KBr): 3090, 2878, 1622 (C=N), 1570, 1280, 835, 702 cm^{-1}. UV−vis: λ_{max} (THF) 424 nm, ϵ = 15 500 M^{-1} cm^{-1}. Anal. Calcd for $C_{36}H_{36}N_2O_6S$: C, 69.21; H, 5.81; N, 4.48; S, 5.13. Found: C, 68.41; H, 5.42; N, 4.44.

Polymerization of 1,5-Bis(2-(2-methoxyethoxy)ethoxy)anthraquinone (EO$_2$AQ) and *p*-Phenylenediamine. Yield, %: 100 (red solid). ^{1}H-NMR, δ (CDCl$_3$, 25 °C): 3.11 (s, 6H), 3.35 (m, 4H), 3.33 (m, 4H), 3.47 (m, 4H), 3.86 (b, 4H), 6.80 (b, 4H), 7.45 (b, 4H), 7.81 (m, 2H). IR (KBr): 3066, 2871, 1613 (C=N), 1564, 1223, 839, 695 cm^{-1}. UV−vis: λ_{max} (CHCl$_3$) 447 nm, ϵ = 6100 M^{-1} cm^{-1}. Anal. Calcd for $C_{30}H_{32}N_2O_6$: C, 69.78; H, 6.20; N, 5.42. Found: C, 67.86; H, 5.62; N, 4.80.

Polymerization of 1,5-Bis(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)anthraquinone (EO$_3$AQ) and 4,4′-Thiodianiline. Yield, %: 96.4 (bright yellow solid). ^{1}H-NMR, δ (CDCl$_3$, 25 °C): 3.15 (bs, 4H), 3.33 (s, 6H), 3.55 (m, 16H), 3.85 (b, 4H), 6.81 (m, 4H), 7.19 (d, 4H), 7.45 (t, 2H), 7.85 (d, 2H). IR (KBr): 3090, 2890, 1616 (C=N), 1570, 1280, 820, 780 cm^{-1}. UV−vis: λ_{max} (THF) 412 nm, ϵ = 24 500 M^{-1} cm^{-1}. Anal. Calcd for $C_{40}H_{44}N_2O_8S$: C, 67.40; H, 6.22; N, 3.93; S, 4.50. Found: C, 65.15; H, 6.29; N, 4.66.

Polymerization of 1,5-Bis(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)anthraquinone (EO$_3$AQ) and *p*-Phenylenediamine. Yield, %: 91.8 (red solid). ^{1}H-NMR, δ (CDCl$_3$, 25 °C): 3.30 (s, 6H), 3.45 (m, 16H), 3.55 (t, 4H), 4.10 (b, 4H), 6.81 (m, 4H), 7.19 (d, 2H), 7.45 (bs, 2H), 7.90 (d, 2H). IR (KBr): 2870, 1618 (C=N), 1565, 1461, 1260, 1105, 793 cm^{-1}. UV−vis: λ_{max} (THF) 460 nm, ϵ = 13 500 M^{-1} cm^{-1}. Anal. Calcd for $C_{34}H_{40}N_2O_8$: C, 67.52; H, 6.68; N, 4.60. Found: C, 64.10; H, 6.53; N, 5.47.

Polymerization of 1,5-Bis(octyloxy)anthraquinone (15OOAQ) and 4,4′-Thiodianiline. Yield, %: 100 (red solid). ^{1}H-NMR, δ (CDCl$_3$, 25 °C): 0.87 (s, 6H), 1.25 (b, 22H), 3.15 (bm, 6H), 6.69 (d, 2H), 6.80 (d, 4H), 7.15 (d, 4H), 7.45 (t, 2H), 7.77 (d, 2H). IR (KBr): 3070, 2945, 2852, 1620 (C=N), 1567, 1280, 1080, 785 cm^{-1}. UV−vis: λ_{max} (THF) 424 nm, ϵ = 8500 M^{-1} cm^{-1}. Anal. Calcd for $C_{42}H_{48}N_2O_2S$: C, 78.22; H, 7.50; N, 4.34; S, 4.97. Found: C, 74.93; H, 7.17; N, 4.53.

Polymerization of 1,5-Bis(octyloxy)anthraquinone (15OOAQ) and *p*-Phenylenediamine. Yield, %: 95.3 (red solid). ^{1}H-NMR, δ (CDCl$_3$, 25 °C): 0.87 (s, 6H), 1.24 (b, 22H), 3.45 (bm, 6H), 6.69 (d, 2H), 6.80 (bm, 2H), 7.05 (d, 2H), 7.45 (t, 2H), 7.77 (d, 2H). IR (KBr): 3055, 2945, 2852, 1618 (C=N), 1566, 1458, 1279, 1050, 785 cm^{-1}. UV−vis: λ_{max} (THF) 446 nm, ϵ = 13 500 M^{-1} cm^{-1}. Anal. Calcd for $C_{36}H_{44}N_2O_2$: C, 80.56; H, 8.56; N, 5.22. Found: C, 80.35; H, 8.37; N, 5.75.

Polymerization of 1,4-Bis(octyloxy)anthraquinone (14OOAQ) and 4,4′-Thiodianiline. Yield, %: 100 (red solid). ^{1}H-NMR, δ (CDCl$_3$, 25 °C): 0.87 (s, 6H), 1.25 (b, 18H), 1.43 (s, 4H) 3.20 (bm, 6H), 6.69 (bs, 2H), 6.98 (bs, 4H), 7.20 (bs, 4H), 7.50 (bs, 2H), 8.20 (bs, 2H). IR (KBr): 3070, 2945, 2852, 1620 (C=N), 1579, 1460, 1280, 1120, 705 cm^{-1}. UV−vis: λ_{max} (THF) 398 nm, ϵ = 14 500 M^{-1} cm^{-1}. Anal. Calcd for $C_{42}H_{48}N_2O_2S$: C, 78.22; H, 7.50; N, 4.34; S, 4.97. Found: C, 78.51; H, 7.70; N, 4.38.

Polymerization of 1,4-Bis(octyloxy)anthraquinone (14OOAQ) and *p*-Phenylenediamine. Yield, %: 100 (red solid). ^{1}H-NMR, δ (CDCl$_3$, 25 °C): 0.87 (s, 6H), 1.25 (b, 18H), 1.43 (s, 4H) 3.50 (bm, 6H), 6.69 (bs, 2H), 6.98 (bs, 4H), 7.20 (s, 4H), 7.50 (bs, 2H), 8.10 (bs, 2H). IR (KBr): 3070, 2945, 2852, 1617 (C=N), 1574, 1463, 1276, 1120, 800 cm^{-1}. UV−vis: λ_{max} (THF) 428 nm, ϵ = 8300 M^{-1} cm^{-1}. Anal. Calcd for $C_{36}H_{44}N_2O_2$: C, 80.56; H, 8.26; N, 5.22. Found: C, 78.34; H, 7.45; N, 5.66.

Polymerization of 2,6-Bis(octyloxy)anthraquinone (26OOAQ) and 4,4′-Thiodianiline. Yield, %: 100 (red solid). ^{1}H-NMR, δ (CDCl$_3$, 25 °C): 0.85 (s, 6H), 1.32 (b, 18H), 1.8 (bs, 4H), 3.4 (bs, 2H), 4.1 (bs, 4H) 6.69 (m, 2H), 6.90 (d, 4H), 7.20 (m, 4H), 7.3 (d, 2H), 7.90 (d, 2H). IR (KBr): 2916, 2852, 1620 (C=N), 1589, 1078, 829 cm^{-1}. UV−vis: λ_{max} (THF) 424 nm, ϵ = 7050 M^{-1} cm^{-1}. Anal. Calcd for $C_{42}H_{48}N_2O_2S$: C, 78.22; H, 7.50; N, 4.34; S, 4.97. Found: C, 76.62; H, 7.16; N, 4.36.

Polymerization of 2,6-Bis(octyloxyanthraquinone (26OOAQ) and *p*-Phenylenediamine. Yield, %: 100 (red solid). ^{1}H-NMR, δ (CDCl$_3$, 25 °C): 0.85 (bs, 6H), 1.35 (b, 18H), 1.43 (m, 4H) 4.15 (bs, 6H), 6.75 (bm, 2H), 7.0 (bs, 2H), 7.45 (dd, 2H), 7.80 (bs, 2H), 8.25 (d, 2H). IR (KBr): 3070, 2945, 2852, 1620 (C=N), 1579, 1460, 1280, 1120, 705 cm^{-1}. UV−vis: λ_{max} (THF) 472 nm, ϵ = 800 M^{-1} cm^{-1}. Anal. Calcd for $C_{36}H_{44}N_2O_2$: C, 80.56; H, 8.26; N, 5.22. Found: C, 77.98; H, 8.10; N, 5.34.

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Supporting Information Available: ^{1}H-NMR spectra of EO$_2$AQ and DEO$_n$AQ (1 page). Ordering information is given on any current masthead page.

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