Palladium-Catalyzed Synthesis of Pure, Regiodefined Polymeric Triarylamines

Felix E. Goodson, Sheila I. Hauck, and John F. Hartwig*

Contribution from the Department of Chemistry, Yale University, P.O. Box 208107, New Haven, Connecticut 06520-8107

Received March 1, 1999

Abstract: Triarylamine polymers were prepared by palladium-catalyzed amination of aryl halides, and the electrochemical and magnetic properties of these materials were studied. Through a careful evaluation of the catalytic and polymer chemistry involved in this process, triarylamine polymers that are exclusively linear and free of phosphorus impurity in the polymer chain have been prepared. To suppress molecular weight-limiting side reactions from palladium-catalyzed poly(*N*-arylaniline) polymerizations, a number of phosphines were screened in reactions of small molecules to form triarylamines. Of these phosphines, tris(*o*-methoxymethylphenyl)phosphine (**7**) and tri(*tert*-butyl)phosphine (**8**) led to quantitative amination without ligand arylation, aryl bromide hydrodehalogenation, or exchange of phosphine aryl groups with the aryl bromide. When these phosphines were used in polymerizations, significant improvements in molecular weights were observed, but an additional molecular weight limiting side reaction, the formation of cyclic oligomers, was not affected. Strategies to minimize cyclizations that compete with chain growth were explored, including the use of oligomeric monomers that greatly reduced the formation of cyclic oligomers. A chromatographic method completely removed low molecular weight cyclic oligomers. A number of poly(*N*-arylaniline) derivatives with M_w values as high as 10^5 g/mol were synthesized by using the optimized palladium-catalyzed method, and the electronic and magnetic properties of these materials were investigated by cyclic voltammetry, magnetic susceptibility, and EPR spectroscopy.

Introduction

Since the discovery in 1985 that doped polyaniline is capable of conducting electricity in the metallic regime,[1] research has focused on using this material in applications such as electrodes in lightweight batteries[2,3] and as flexible, hole-transport layers in electroluminescent devices.[4,5] Particularly appealing aspects of this material are the simple and inexpensive synthesis by chemical[6] or electrochemical[7−9] oxidation of aniline and the moisture and air stability of its conductive form.[1] Although dominated by para regiochemistry, it is likely that ortho and meta defects as well as biphenyl defects formed by C−C coupling occur uncontrollably during the synthesis of this material.[10] Furthermore, the derivatives of this material that can be formed by the aniline oxidation are limited. Derivatives with substituents on the aromatic rings have been prepared,[11−14] but these substituents create further structural ambiguity during the electrophilic polymerization because their directing properties may counteract the para-directing property of the amino group.

Poly(*m*-aniline)[15−19] and oligomeric aniline derivatives with alternating meta and para regiochemistry[20] have been presented recently as possible candidates for organic ferromagnetic applications. Derivatives of poly(*m*-aniline) have been synthesized by the copper-mediated Ullmann coupling.[15,19] However, these polymerizations are accompanied by the formation of insoluble fractions, which may have resulted from cross-linking.[16]

A general method to prepare a variety of aniline derivatives would allow one to optimize and tune the properties of arylamine polymers. Recent research by our group[21,22] and Buchwald's[23−25] has led to a highly efficient synthesis of tertiary

---

[1] MacDiarmid, A. G.; Chiang, J.-C.; Halpern, M.; Huang, W.-S.; Mu, S.-L.; Somasiri, N. L. D.; Wu, W.; Yaniger, S. I. *Mol. Cryst. Liq. Cryst.* **1985**, *121*, 173.

[2] MacDiarmid, A. G.; Mu, S. L.; Somasiri, M. L. D.; Wu, W. *Mol. Cryst. Liq. Cryst.* **1985**, *121*, 187.

[3] Kitani, A.; Kaya, M.; Sasaki, K. *J. Electrochem. Soc.* **1986**, *133*, 1069.

[4] Gustafsson, G.; Cao, Y.; Treacy, G. M.; Klavetter, F.; Colaneri, N.; Heeger, A. J. *Nature* **1992**, *357*, 477.

[5] Yang, Y.; Westerweele, E.; Zhang, C.; Smith, P.; Heeger, A. J. *J. Appl. Phys.* **1995**, *77*, 694.

[6] Abe, M.; Ohtani, A.; Umemoto, Y.; Akizuki, S.; Ezoe, M.; Higuchi, H.; Nakamoto, K.; Okuno, A.; Noda, Y. *J. Chem. Soc., Chem. Commun.* **1989**, 1736.

[7] Mizoguchi, T.; Adams, R. N. *J. Am. Chem. Soc.* **1962**, *84*, 2058.

[8] Mohilner, D. M.; Adams, R. N.; Argersinger, W. J. *J. Am. Chem. Soc.* **1962**, *84*, 3618.

[9] Diaz, A. F.; Logan, J. A. *J. Electroanal. Chem.* **1980**, *11*, 111.

[10] Yoshizawa, K.; Ito, A.; Tanaka, K.; Yamabe, T. *Synth. Met.* **1992**, *48*, 271.

[11] Wei, X.-L.; Wang, Y. Z.; Long, S. M.; Bobeczko, C.; Epstein, A. J. *J. Am. Chem. Soc.* **1996**, *118*, 2545.

[12] Mattoso, L. H. C.; Faria, R. M.; Bulhões, L. O. S.; MacDiarmid, A. G. *J. Polym. Sci., Polym. Chem. Ed.* **1994**, *32*, 2147.

[13] Wei, Y.; Hariharan, R.; Patel, S. A. *Macromolecules* **1990**, *23*, 758.

[14] Leclerc, M.; Guay, J.; Dao, L. H. *Macromolecules* **1989**, *22*, 649.

[15] Ito, A.; Ota, K.; Tanaka, K.; Yamabe, T.; Yoshizawa, K. *Macromolecules* **1995**, *28*, 5618.

[16] Yoshizawa, K.; Ito, A.; Tanaka, K.; Yamabe, T. *Solid State Commun.* **1993**, *87*, 935.

[17] Yoshizawa, K.; Takata, A.; Tanaka, K.; Yamabe, T. *Polym. J.* **1992**, *24*, 857.

[18] Yoshizawa, K.; Tanaka, K.; Yamabe, T. *Chem. Lett.* **1990**, 1311.

[19] Ishida, T.; Iwamura, H. *Chem. Lett.* **1991**, 317.

[20] Wienk, M. M.; Janssen, R. A. J. *J. Am. Chem. Soc.* **1997**, *119*, 4492.

[21] Louie, J.; Hartwig, J. F. *Tetrahedron Lett.* **1995**, *36*, 3609.

[22] Hartwig, J. F. *Synlett* **1997**, 329.

[23] Wolfe, J. P.; Buchwald, S. L. *J. Org. Chem.* **1996**, *61*, 1133.

[24] Guram, A. S.; Rennels, R. A.; Buchwald, S. L. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1348.

10.1021/ja990632p CCC: $18.00

aromatic amines from primary or secondary amines and aryl bromides. In addition, studies by workers at Tosoh in Japan have revealed a system for formation of tertiary amines that provides yields and turnover numbers that are appropriate for commercial applications.[26,27]

During the past two years, several research groups have published the preparation of polymeric aryl- and diarylamines. However, these reports contain little information on the purity of the polymers produced from this chemistry or information on why one catalyst system provides different results from another. For example, small-molecule model studies were not reported that would reveal minor side products, and evaluation of whether linear, ligand-free polymer was formed was not presented. Kanbara used the palladium-mediated amination chemistry to develop a synthesis of poly(aryleneamines) with alkyl spacers in the polymer backbone[28,29] and has reported polymeric triarylamines with attached chromophores.[30,31] Kanbara[32] and Meyer[33] have independently reported the synthesis of parent poly(*m*-aniline), and Meyer has shown that these polymers contain some cross-linking and BINAP ligand. Buchwald prepared and studied the electrochemistry of pure, discrete, oligomeric models for poly(*p*-aniline).[34,35]

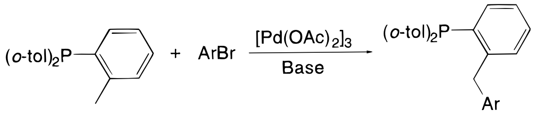
Our group has studied triarylamine materials and we have reported discrete oligomers[36] and dendrimers[37] that show interesting magnetic and electronic properties. As small molecules, triarylamines have particularly interesting electronic and magnetic properties. They generate some of the most stable radical cations, and they are readily oxidized to this aminium state. Because of these properties, triarylamines have been valuable for hole transport layers in LED applications and have been used to observe high-spin polyradicals. Polymeric triarylamines should combine the chemical properties of the small molecules with the physical properties of macromolecules, while providing a number of advantages over polyanilines that have secondary arylamine linkages. For example, triarylamine macromolecules should form more stable radicals than analogous diarylamines or carbon-based radicals, considering their higher stability as small molecules.[38,39] Further, a few studies suggest that triarylamines may have conductive properties that are similar to those of poly(*p*-aniline),[40] and in these cases one could tune the electronic properties of the nitrogen and perhaps control solid-state structures by using appropriate functionality on the *N*-aryl substituent. Finally, a preparation of triarylamine polymers by C−N bond formation would eliminate the possibility of forming cross-linked polymer and may, therefore, generate unambiguously linear material.

In communication form,[41] we have reported that palladium-mediated aminations could generate donor−acceptor triarylamine copolymers in high yields and moderate molecular weight, and poly(*N*-arylaniline) materials with molecular weights near 5000. These polymerizations underwent three molecular weight limiting events. First, CH activation of the tolyl groups on the tri(*o*-tolyl)phosphine ligands[42] used in the amination reaction resulted in incorporation of phosphorus atoms into the polymer chains, and most likely led to end-capping of the chains by phosphines and by hydrogen atoms. Second, hydrodehalogenation of the aryl halide led polymer end-capping and limited the scope of polymer that could be prepared with high molecular weight to those produced from electron-poor aryl bromide monomers. Third, cyclization of intermediate oligomers competed with chain growth. This cyclization reduced the molecular weights of the polymer samples and broadened the molecular weight distributions.

In this paper, we present studies that overcome these limitations on the palladium-catalyzed synthesis of triarylamine polymers and our success in generating polymers that are free of cyclic oligomers and of phosphorus in the polymer chain, even when electron-rich aryl bromides are involved. Amination reactions on small molecules were used to find ligands that would minimize phosphine incorporation and aryl halide hydrodehalogenation. In addition, strategies were followed to reduce the impact of competing cyclization by using oligomeric monomers. Alternatively, we found that Sephadex chromatography would remove cyclic oligomers. These studies led to the isolation of polymer that is free of phosphorus and cyclic oligomer. With pure polymer in hand, we obtained preliminary electronic and magnetic characterization of selected examples of the polymeric triarylamines.

Results and Discussion

Effect of Ligand on Amination of Electron-Poor Aryl Bromides. It is well-known that quantitative condensation reactions are required to produce high molecular weight polymers by a step growth mechanism. Thus, improvements on the preparation of triarylamine polymers has relied upon our ability to prevent phosphine arylation (eq 1)[41−44] and aryl halide hydrodehalogenation processes[45] that occur in the palladium-catalyzed amination to form triarylamines. Initially, we sought a phosphine with similar activity to tri(*o*-tolyl)phosphine (**1**) that lacked the *o*-methyl C−H bonds that undergo phosphine arylation. In rough initial studies, we found that reactions involving tris(*o*-methoxyphenyl)phosphine as ligand were slug-



(1)

---

[25] Marcoux, J.-F.; Wagaw, S.; Buchwald, S. L. *J. Org. Chem.* **1997**, *62*, 1568.

[26] Nishiyama, M.; Yamamoto, T.; Koie, Y. *Tetrahedron Lett.* **1998**, *39*, 617.

[27] Yamamoto, T.; Nishiyama, M.; Koie, Y. *Tetrahedron Lett.* **1998**, *39*, 2367.

[28] Kanbara, T.; Honma, A.; Hasegawa, K. *Chem. Lett.* **1996**, 1135.

[29] Kanbara, T.; Izumi, K.; Narise, T.; Hasegawa, K. *Polym. J.* **1998**, *30*, 66.

[30] Kanbara, T.; Imayasu, T.; Hasegawa, K. *Chem. Lett.* **1998**, 709.

[31] Kanbara, T.; Oshima, M.; Imayasu, T.; Hasegawa, K. *Macromolecules* **1998**, *31*, 8725.

[32] Kanbara, T.; Izumi, K.; Nakadani, Y.; Narise, T.; Hasegawa, K. *Chem. Lett.* **1997**, 1185.

[33] Spetseris, N.; Ward, R. E.; Meyer, T. Y. *Macromolecules* **1998**, *31*, 3158.

[34] Singer, R. A.; Sadighi, J. P.; Buchwald, S. L. *J. Am. Chem. Soc.* **1998**, *120*, 213.

[35] Sadighi, J. P.; Singer, R. A.; Buchwald, S. L. *J. Am. Chem. Soc.* **1998**, *120*, 4960.

[36] Louie, J.; Hartwig, J. F. *Macromolecules* **1998**, *31*, 6737.

[37] Louie, J.; Hartwig, J. F.; Fry, A. J. *J. Am. Chem. Soc.* **1997**, *119*, 11695.

[38] Tris(4-bromophenyl)aminium hexachloroantimonate is stable enough to be sold commercially (Aldrich).

[39] Chow, Y. L. In *Reactive Intermediates*; Abramovitch, R. A., Ed.; Plenum Press: New York, 1980; Vol. 1, pp 151−262.

[40] Ishikawa, M.; Kawai, M.; Ohsawa, Y. *Synth. Met.* **1991**, *40*, 231.

[41] Goodson, F. E.; Hartwig, J. F. *Macromolecules* **1998**, *31*, 1700.

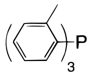
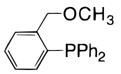
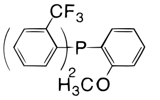
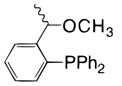
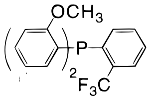
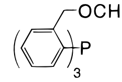
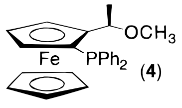
[42] Louie, J.; Hartwig, J. F. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 2359.

[43] Beller, M.; Fischer, H.; Herrmann, W. A.; Öfele, K.; Brossmer, C. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1848.

[44] Herrmann, W. A.; Brossmer, C.; Öfele, K.; Reisinger, C.-P.; Priermeier, T.; Beller, M.; Fischer, H. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1844.

[45] Hartwig, J. F.; Richards, S.; Barañano, D.; Paul, F. *J. Am. Chem. Soc.* **1996**, *118*, 3626.

Table 1. Screening of Phosphines for Amination of Electron-Poor Aryl Halides

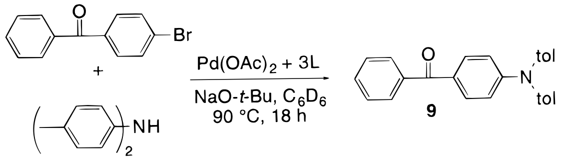
Ligand	*%Yield* [a]	*Ligand*	*%Yield* [a]
 **(1)**	93	 **(5)**	94
 **(2)**	89	 **(6)**	91
 **(3)**	97	 **(7)**	98 (94)
 **(4)**	84	$(t\text{-Bu})_3$P **(8)**	98 (96)

[a] Determined by ^{1}H NMR integrations relative to a 1,3,5-trimethoxybenzene internal standard. Values in parentheses reflect isolated yields. Reported values are the average of at least two trials.

gish, while reactions containing tris[*o*-(trifluormethyl)phenyl]phosphine as ligand did not run to completion when using 5 mol % catalyst. We conjectured that the methoxyphenyl phosphine bound too strongly to the metal and that the trifluoromethylphenyl phosphine bound too weakly. Therefore, we prepared mixed phosphines **2** and **3** shown in Table 1 in the hopes of obtaining a ligand with intermediate binding ability that would give better results.

During the course of this work, a number of groups published results with different ligands that improved the yields of various palladium-catalyzed amination reactions. In particular, Buchwald showed that the amination with acyclic secondary alkylamines was improved when Kumada's ligand **4** was used.[25] We were intrigued with this result, but the expense of **4** limited its practicality. Thus we prepared the more readily available **5**,[46] **6**,[47] and **7**[48] (Table 1). Very recently, Nishiyama, Yamamoto, and Koie showed that the use of tri(*tert*-butyl)phosphine (**8**) gave high yields and turnover numbers in the formation of *N*-arylpiperazines[26] and triarylamines.[27]

To test if these phosphines would be suitable for formation of triarylamine polymers in the absence of concomitant phosphine arylation, we attempted the amination of 4-bromobenzophenone with ditolylamine using accurate 1:1 ratios of the reagents and a combination of the various phosphines and palladium acetate to form triarylamine **9** (eq 2). Reactions were conducted in benzene-d_6, and the yields of **9** were evaluated with respect to a trimethoxybenzene internal standard. For the phosphines that gave the most promising results, isolated yields were also obtained. The results of these experiments are presented in Table 1. These data show that **1** does promote the reaction in good yield, but the reactions are not quantitative. One of the mixed phosphines **2**, Kumada's ligand **4**, and two of the analogues of **4**, ligands **5** and **6**, gave good yields, but they were lower than those for reactions involving **1**. In contrast, reactions containing the phosphines **3**, **7**, and **8** gave essentially quantitative yield. Pure product **9** was isolated in about 95% yield in these cases. These results suggested that **3**, **7**, and **8** are good candidates for polymerizations that form polymeric triarylamines.



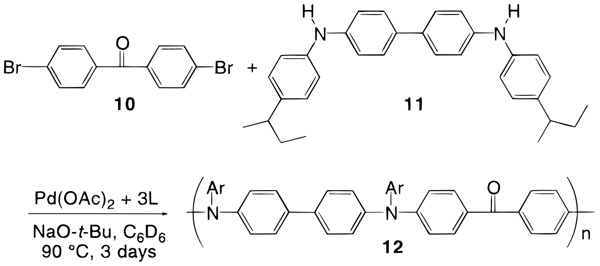
(2)

Table 2. Polymerization Results with Electron-Poor Aryl Bromide Monomers[a]

entry	phosphine	concn,[b] M	% yield[c]	M_n[d]	M_w[e]	M_p[f]
1	**1**	1	87	8400	28800	24300
2	**3**	1	60	12600	61100	49400
3	**7**	1	60	11500	71500	56100
4	**8**	1	88	14900	88000	88100
5	**1**	0.25	82	8400	41400	43600
6	**8**	0.25	83	11500	123500	116200

[a] Polymerizations were run for 3 days at 90 °C in benzene with a catalyst loading of 2% (Pd/Br) and 3 equiv of phosphine per palladium. Listed values are the average of at least two trials. Molecular weights were measured by GPC and reported values are relative to polystyrene standards. [b] Approximate concentration determined by mmol of each monomer per mL of solvent. [c] Nonquantitative yields were due to gel formation. [d] Number-averaged molecular weight. [e] Weight-averaged molecular weight. [f] Molecular weight at peak maximum.

Polymerizations with Electron-Poor Aryl Bromides. Polymerizations were carried out between 4,4′-dibromobenzophenone **10** and diaminobiphenyl monomer **11** to form polymer **12** (eq 3) with various phosphines and at varied concentrations.



(3)

The results are presented in Table 2. Although the data indicate only a marginal increase in number-averaged molecular weight with use of the new phosphines, weight-averaged molecular weights, as well as molecular weight at the maximum intensity of the GPC trace (peak molecular weight), were improved dramatically. Phosphine **8** provided the highest molecular weight data. As mentioned in the Introduction, we have shown previously for polymerizations using P(*o*-tolyl)$_3$ as ligand that coupling to form macrocyclic products can compete with linear chain growth. The macrocyclic products were identified by both MALDI MS of crude polymer samples and isolation of a macrocyclic product from a reaction under high dilution conditions.[41] The increase in M_w but small change in M_n in the polymerizations using phosphine **8** is consistent with increased yields of the amination reaction with little effect on the competing cyclization. As a result, peak molecular weight increases, but low molecular weight spikes due to cyclic oligomers are unchanged, creating a broader molecular weight distribution. This effect can be seen in Figure 1, which shows the chromatograms for polymers formed with phosphines **1** and **8** (Table 2, entries 1 and 4). Previously, the polymerization of **10** with a *m*-diaminobenzene monomer showed a marked effect of concentration on molecular weight caused by competing cyclization and chain growth; lower concentrations resulted in lower molecular weights.[41] During the synthesis of **12**, the effect of concentration on molecular weight was less straightforward and appeared to result from two factors. Under dilute conditions (Table 2, entries 5 and 6), the cyclization was more favored

---

(46) Cookson, E. A.; Crofts, P. C. *J. Chem. Soc. C* **1966**, 2003.
(47) Terfort, A.; Brunner, H. *J. Chem. Soc., Perkin Trans. 1* **1996**, 1467.
(48) Letsinger, R. L. *J. Org. Chem.* **1958**, *23*, 1806.

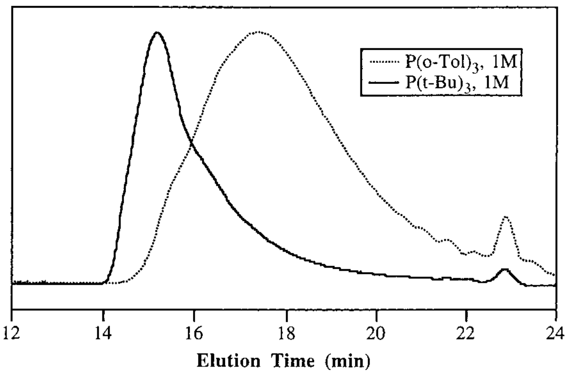


Figure 1. GPC chromatograms for polymer **12** synthesized with phosphines **1** (dotted line) and **8** (solid line).

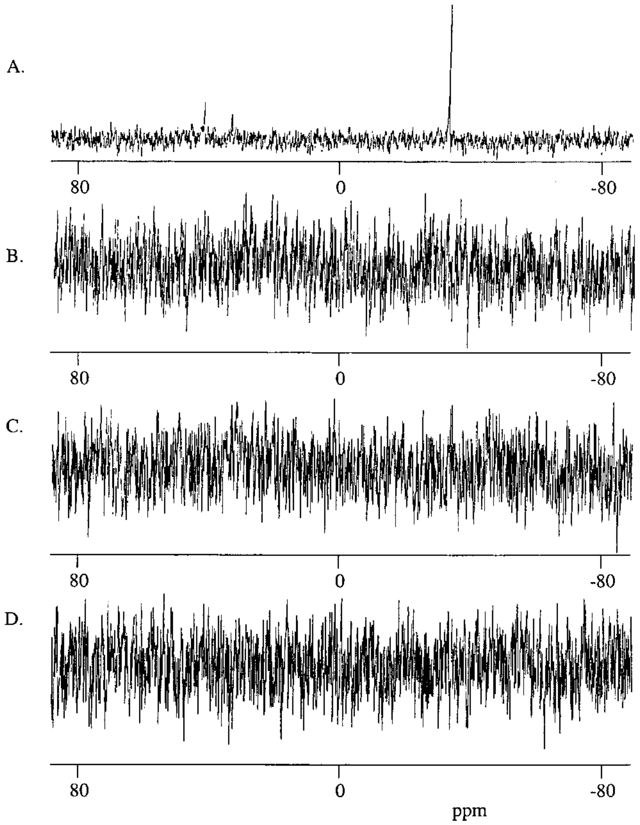


Figure 2. ^{31}P NMR spectra for samples of polymer **12** synthesized with phosphines **1** (A), **3** (B), **7** (C) and **8** (D).

than at high concentrations and the number-averaged molecular weight was slightly lower. However, the reaction appeared to proceed further to completion as evidenced by the higher weight average and peak molecular weights.

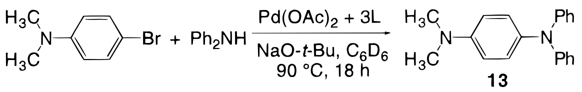
To determine if phosphines **3**, **7**, and **8** were reducing the phosphorus incorporation as designed by eliminating tolyl group arylation, polymer samples that were generated from reactions containing the different ligands were analyzed by ^{31}P NMR after Soxhlet extraction of the samples for 12 h with hexane solvent. As shown in Figure 2, the sample formed using tri-*o*-tolylphosphine as ligand showed a strong signal in the triarylphosphine region, with other weaker signals in the phosphine oxide region of the spectrum. However, we were pleased to find that the polymer generated using ligands **3**, **7**, and **8** showed no detectable ^{31}P signals after data collection for 12 h.

Catalytic Chemistry of Polymerizations Involving Electron-Rich Aryl Halides. Although the above results led to improved polymerizations using dibromobenzophenone, it was unclear if the new phosphines would reduce side reactions during amination of more electron rich aryl halides. In particular, aryl halide dehydrohalogenation occurs to a greater extent during reactions with more electron rich aryl halides,[24,45,49] and polymerizations to form some of our target poly(*N*-arylaniline)s would involve coupling of electron-rich oligomers containing aryl halide termini. To evaluate the ligands for such polymerizations, we again conducted reactions with model substrates. In this case, the reaction of (*N*,*N*-dimethylamino)-4-bromobenzene with diphenylamine to form triarylamine **13** (eq 4) was used as a model. Reactions were again run in deuterated solvent, and yields were determined by NMR spectrometry. Isolated yields were obtained for the most promising candidates, and the results are listed in Table 3.

Table 3. Screening of Phosphines for Amination of Electron-Rich Aryl Halides

phosphine	% yield[a]	% arene[a]	phosphine	% yield[a]	% arene[a]
1	85	12	**5**	60	15
2	68	*b*	**6**	59	17
3	85	trace	**7**	94 (88)	6
4	77	trace	**8**	97 (88)	

[a] Determined by ^{1}H NMR integrations relative to a 1,3,5-trimethoxybenzene internal standard. Values in parentheses reflect isolated yields. Reported values are the average of at least two trials. [b] A number of products were formed with overlapping resonances.



13

(4)

Two of the phosphines showed improved results relative to tri-*o*-tolylphosphine **1**. Reactions containing either phosphine **7** or **8** gave triarylamine **13** in significantly higher yields than those employing **1**, and these yields were close enough to quantitative to warrant investigation in polymerization studies. No hydrodehalogenation was detectable when **8** was used as the ligand. The crude NMR spectra for reactions of **7** and **8** were spectacularly clean; the 88% isolated yields reflect only mechanical losses in isolation. Thus, ligands **7** and **8** were carried forward for the synthesis of polymers discussed in the next section.

The other phosphines showed lower yields, but the reasons for the reduced yields were not always straightforward. For example, Kumada's ligand **4** significantly reduced the amount of arene formed, but the reaction yield was still lower than when **1** was used as ligand. Reactions containing phosphine **2** produced several unidentified byproducts in addition to forming triarylamine **13**. Reactions employing mixed phosphine **3** gave higher yields than did those employing **1**, but the yield was not high enough to generate high molecular weight triarylamine polymer.

An additional problem with Kumada's ligand **4** and the diphenylphosphino benzyl ether ligands **5** and **6** was detected in these studies. Reactions involving **4**, **5**, and **6** produced triphenylamine as a side product observed by GC-MS. This byproduct most likely resulted from exchange of phosphine and palladium-bound aryl groups known to occur in ArPdL$_2$X complexes.[50,51] This aryl group exchange leads to incorporation of phosphorus into the polymer backbone as well as end-capping of the polymer with an aryl group.[52] Thus, the formation of

---

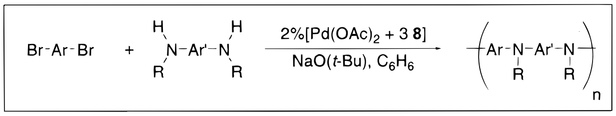
(49) Driver, M. S.; Hartwig, J. F. *J. Am. Chem. Soc.* **1996**, *118*, 7217.
(50) Kong, K.-C.; Cheng, C.-H. *J. Am. Chem. Soc.* **1991**, *113*, 6313.
(51) Goodson, F. E.; Wallow, T. I.; Novak, B. M. *J. Am. Chem. Soc.* **1997**, *119*, 12441.

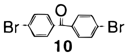
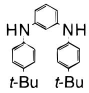
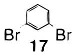
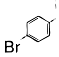
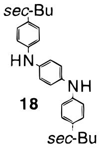
Table 4. Results for the Polymerization of **11** with **14**[a]

phosphine	% cat.[b]	P/Pd[c]	concn,[d] M	% yield	M_n[e]	M_w[f]	M_p[g]
1	2	3	1	79	8900	32100	18400
7	2	3	1	85	16100	45200	42500
8	2	3	1	95	13600	102100	103600
1	2	3	0.25	94	6800	15500	13600
1	2	3	0.125	84	6700	13800	13200
8	2	3	0.25	90	19300	107200	140000
8	2	3	0.125	95	11800	69300	104200
8	0.5	3	0.125	85	11800	65500	89200
8	0.05	3	0.125	78	11700	70300	96900
8	2	6	0.125	93	12600	85200	128600

[a] Polymerizations were run for 3 days at 90 °C in benzene. Listed values are the average of at least two trials. Molecular weights were measured by GPC and reported values are relative to polystyrene standards. [b] Percent catalyst (Pd/Br). [c] Phosphine-to-palladium ratio. [d] Approximate concentration determined by mmol of each monomer per mL of solvent. [e] Number-averaged molecular weight. [f] Weight-averaged molecular weight. [g] Molecular weight at peak maximum.

Table 5. General Polymerization Results[a]

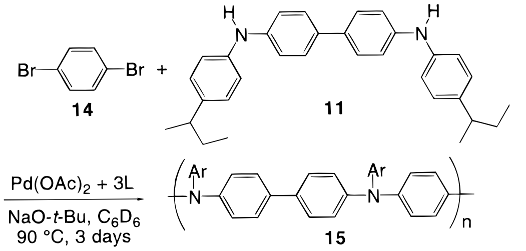


Br−Ar−Br	RHN−Ar'−NHR	*Polymer*	*%Yield*	M_n[b]	M_w[c]	M_p[d]
 **10**	 **16**	**19**	69	18,000	84,900	94,000
 **17**	**16**	**20**	68	7000	106,100	99,290
 **14**	**16**	**21**	63	5800	79,900	65,700
14	 **18**	**22**	83	26,100	98,900	119,900

[a] Polymerizations were run for 3 days at 90 °C in benzene at 1 M concentration with 0.5% Pd/Br catalyst load and 3 phosphines per palladium. Listed values are the average of at least two trials. Molecular weights were measured by GPC and reported values are relative to polystyrene standards. [b] Number-averaged molecular weight. [c] Weight-averaged molecular weight. [d] Molecular weight at peak maximum.

triarylamine, even in the trace amounts that were observed in these reactions, must be prevented if pure polymer is to be obtained.

Polymerizations Involving Electron-Rich Aryl Bromides. To test the viability of phosphines **7** and **8** in actual polycondensations, and to optimize the conditions of the polymerizations, a series of reactions between 1,4-dibromobenzene (**14**) and diaminobiphenylene monomer **11** to form polymer **15** (eq 5) were conducted. In these polymerizations, reaction parameters such as phosphine, substrate concentration, catalyst load, and phosphine-to-palladium ratio were all varied, and the results are listed in Table 4. At 1 M concentration, polymers generated by using either ligand **7** or **8** showed significantly higher molecular weights than those produced by using ligand **1**. Number averaged molecular weights for samples formed with **7** appeared to be slightly higher than those for samples from **8**, although weight-averaged and peak values were higher for the latter. The similarity of reactions involving these two ligands, combined with the commercial availability of **8**, led us to use **8** for the majority of the subsequent polymerization studies.[29]



(5)

The effect of concentration on the molecular weight of polymer **15** appeared to result from the same competing factors as it did in the synthesis of polymer **12** (vide supra). When **8** was used as the phosphine, optimal molecular weights for this polymer were obtained at 0.25 M concentration (entry 6). The other variables mentioned above appeared to have little effect on polymer molecular weight. Catalyst loadings as low as 0.05% gave polymers with high molecular weights and facilitated catalyst removal from the crude polymer upon workup. The molecular weight was insensitive to the phosphine-to-palladium ratio (entry 10) and to the use of either arene or dioxane solvent.

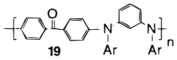
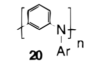
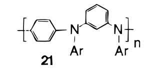
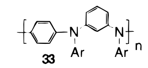
Given these results, it appeared that a combination of Pd$(OAc)_2$ and **8** as catalyst was ideal for the synthesis of both electron-rich and electron-poor polymers in good yields and with high molecular weights. To test the generality of this system and to obtain a route into a series of poly(*N*-arylanilines), polymerizations were performed using a variety of monomers, and the results are presented in Table 5. The donor/acceptor copolymer **19** was formed in good yield with a number-averaged molecular weight of almost 20000. Samples of meta, and alternating meta−para poly(*N*-arylaniline) **20** and **21** were prepared with very high weight-averaged and peak molecular weights, although the number-averaged values were reduced by formation of cyclic oligomer.

Formation of cyclic oligomers was confirmed by mass spectrometry and the amount of this cyclic material depended on the regiochemistry of the arylene moieties. As noted in our previous report,[41] the *p*-poly(*N*-arylaniline) material **22** is less susceptible to cyclization than are the isomeric versions containing meta linkages. This assertion is supported by the higher molecular weight data and the absence of GPC peaks due to oligomeric material. The identity of the peaks due to oligomers in the GPC traces of polymerizations involving *m*-phenylene units was corroborated by MALDI mass spectrometry. In the case of an A_2B_2 polymerization reaction, such as that between a *m*-dibromobenzene and *N*-aryl phenylene diamines, linear oligomers can contain an unequal number of the two monomers, but cyclic oligomers would have only an equal number of the two monomers. In the case of an AB polymerization odd or even numbers of monomers would be present in the cyclic or oligomeric linear material. MALDI MS analysis of the crude samples from the reaction of **14** with **16** or the reaction of **17** with **16** in Table 5 showed only oligomers containing an equal number of the two monomer units. For example, peaks due to the proton adducts of tetramer, hexamer, octamer, decamer, etc. were observed in both cases, but peaks due to trimer, pentamer, etc. were not observed. To confirm the appropriateness of the MALDI MS analysis, the polymer formed by condensation of *N*-aryl-3-bromoaniline to form polymer **20** in Table 6 was subjected to MALDI MS and showed the presence of oligomers containing both odd and even numbers of monomers.

---

(52) Goodson, F. E.; Wallow, T. I.; Novak, B. M. *Macromolecules* **1998**, *31*, 2047.

Table 6. Removal of Cyclic Oligomers by Sephadex Filtration

		Before Filtration			*After Filtration*		
Polymer	*Yield*	M_n	M_w	M_p	M_n	M_w	M_p
 **19**	71	18,040	82,679	92,500	49,100	94,800	90,900
 **20**	73	7300	48,200	54,000	22,400	53,900	55,800
 **21**	66	5400	83,000	87,000	25,100	98,700	79,500
 **33** (from oligomeric monomers)	54	15,600	78,700	85,300	34,700	87,500	85,300

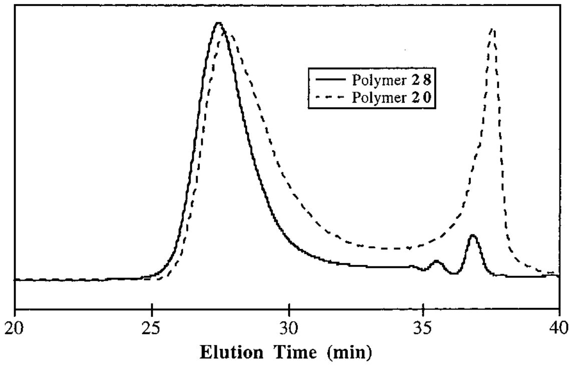


Figure 3. GPC chromatograms for polymer **20** (dotted line), formed with monomeric monomers, and polymer **28** (solid line), formed from pentameric monomers.

Overall, we have demonstrated that P(t-Bu)$_3$ and the P,O ligand **7** eliminates the problem of phosphorus incorporation into the polymer, and P(t-Bu)$_3$ greatly reduces aryl bromide hydrodehalogenation, thereby producing triarylamine polymers with number-averaged molecular weights greater than 25000. This value corresponds to chains that are, on average, over 100 arylamine units in length.

Strategies To Eliminate Competing Cyclization. The dashed line in Figure 3 presents the GPC chromatogram for polymer **20**. This trace contains a sharp spike that corresponds to a cyclic tetramer (as determined by MALDI mass spectrometry). We reasoned that polymerizations initiated with "monomers" that were already five arylamine units in length could not form the cyclic tetramer and might significantly reduce the formation of the cyclic oligomers. Therefore, we developed the route in Scheme 1 to bromo- and amino-terminated pentameric monomers. Diaminomonomer **23** was simply reacted in 1,3-dibromobenzene solvent using a combination of palladium acetate and DPPF (bis(diphenylphosphino)ferrocene)[49] as catalyst to form dibromotrimer **24** in 78% yield after distillation of the excess dibromobenzene and column chromotography of the residue. This material was transformed into the diaminotrimer **25** via amination with an excess of the appropriate aniline derivative. Treatment with acid to extract excess aniline and column chromotography of the material remaining in the organic layer gave **25** in 89% yield. These simple procedures were repeated to yield the dibromopentamer **26** and diaminopentamer **27** in 80% and 89% isolated yields.

Reaction of **26** and **27** in the presence of NaO-t-Bu as base and a combination of 0.5% Pd(OAc)$_2$ and phosphine **8** as catalyst precursor produced meta poly(N-arylaniline) derivative **28** in 79% isolated yield with molecular weight data M_n = 12100, M_w = 74800, and M_p = 87100 (average of two experiments). As can be seen from the GPC chromatograms depicted in Figure 3, this strategy did dramatically reduce the amount of cyclic oligomer formed in this polymerization relative to that formed between the two true monomers. A small amount of cyclic oligomer of higher molecular weight was still present, revealing the high propensity of triarylamine oligomers to adopt a conformation that undergoes cyclization. In contrast to the ^{1}H and ^{13}C NMR spectra of polymers prepared from true monomers, the NMR spectra presented in Figure 4 for the polymer **28** prepared from oligomeric monomers are clearly resolved. Thus, the amount of cyclic material is low,[53] and the polymer contains regular, meta regiochemistry.

As discussed above, large amounts of cyclic oligomer were obtained when using simple monomers for the formation of

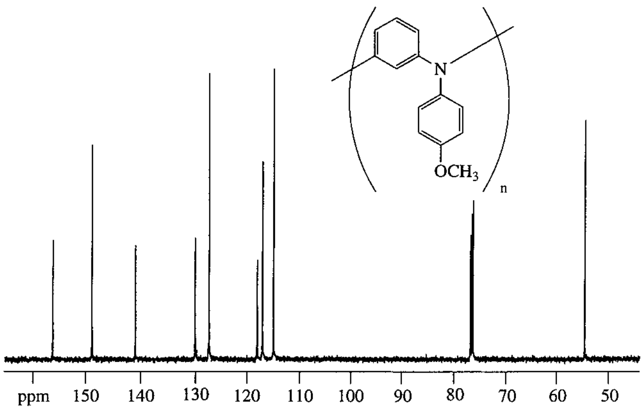
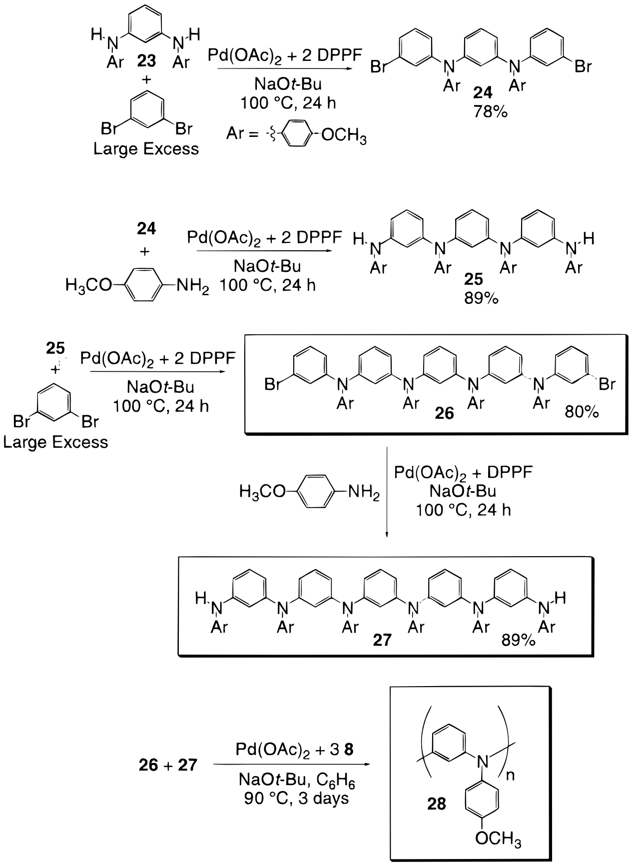


Figure 4. ^{13}C NMR spectrum for polymer **28**.

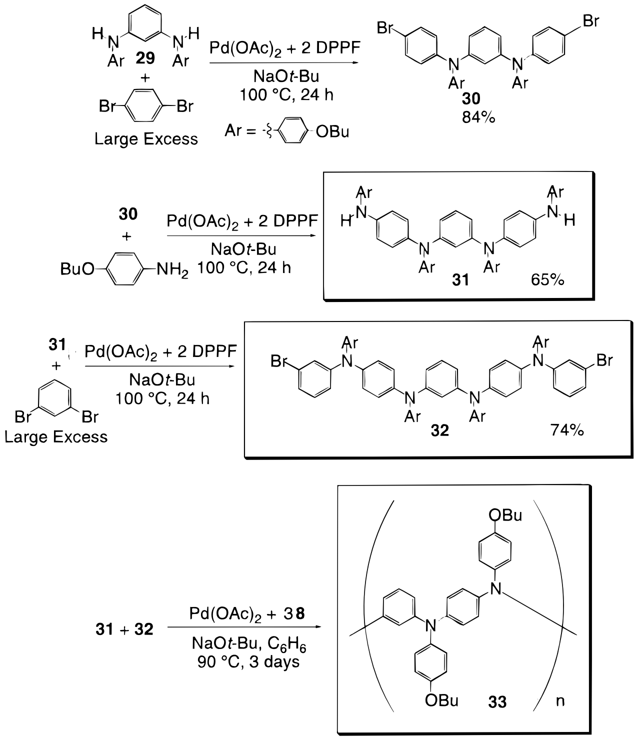
Scheme 1. "Oligomeric Monomer" Strategy for the Synthesis of m-poly(N-arylaniline) **28**



---

[53] High molecular weight cyclic material may display the same NMR spectra as linear polymeric mateiral. Thus, we can conclude that the amount of cyclic oligomer is low, but we cannot comment on the presence or absence of high molecular weight cyclic material.

Scheme 2. "Oligomeric Monomer" Strategy for the Synthesis of Alternating *m*- and *p*-Poly(*N*-arylaniline) **33**



poly(*N*-arylaniline) with alternating meta and para regiochemistry. Thus, the "oligomeric monomer" strategy was also applied to the synthesis of these materials as shown in Scheme 2. Diaminotrimer **31** and dibromopentamer **32** were polymerized under the identical conditions to those described above for **26** and **27** to yield polymer **33** in 71% yield with molecular weight values of $M_n = 14600$, $M_w = 74100$, and $M_p = 84200$ (average of two trials). Monomers with butoxy rather than methoxy substituents were used in this case because the polymer containing methoxy substituents was insoluble. GPC showed that polymer **33** contained much less cyclic oligomer than those produced from true monomers.

Although the "oligomeric monomer" strategy did not completely eliminate formation of cyclic material, it did greatly reduce the quantities of cyclic impurities in the polymer samples and involved the use of discrete oligomers of poly(*N*-arylaniline) derivatives that were prepared without using protecting groups. To obtain material that was completely void of cyclic oligomers, we sought a method to separate linear polymer from cyclic oligomer upon workup. Filtration of the polymer samples through a 12 in. × 1.5 in. column of Sephadex LH-60 SEC resin using THF as eluent removed the low molecular weight cyclic materials. Table 6 gives molecular weight data for specific polymer samples before and after this treatment. The molecular weight distributions for these materials are greater than the 2.0 value of an ideal step-growth polymerization. It is not clear if our molecular weight distribution results from aspects of the palladium chemistry, selective loss of certain molecular weight fractions upon workup, or the presence of high molecular weight cyclic material. Nevertheless, NMR spectra of samples obtained from filtration contained the appropriate number of well-resolved resonances and GPC traces showed the absence of low molecular weight cyclic materials.

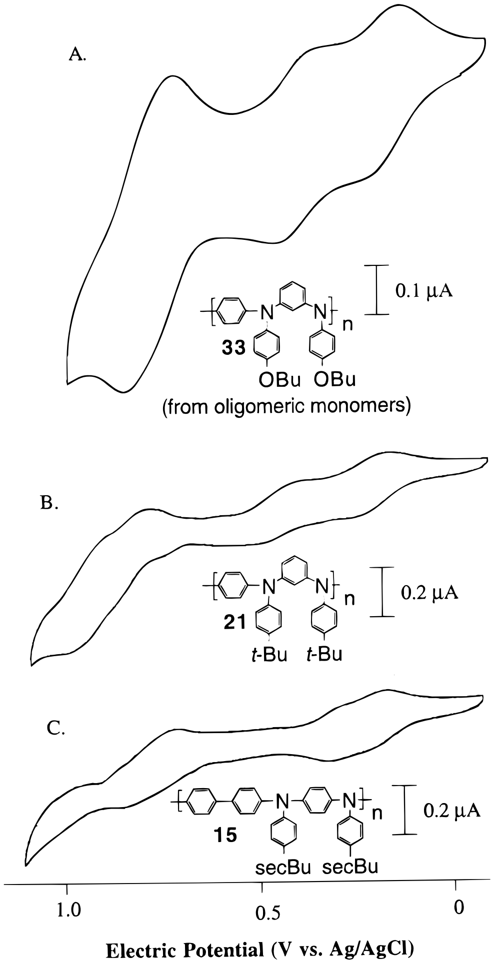


Figure 5. Cyclic voltammograms for (A) polymer **33**, (B) polymer **21**, and (C) polymer **15**.

Cyclic Voltammetry Studies. Alternating meta and para poly(*N*-arylaniline)s **21** and **33** exhibited resolved and reversible cyclic voltammograms (Figure 5). Three distinct redox waves were observed for polymer **33** (Figure 5a) at 0.161, 0.411, and 0.794 V vs Ag/AgCl (calibrated with Fc/Fc$^+$ = 0.178 V). The peak-to-peak separations for the first two waves were 67 and 65 mV, which are very close to the theoretical value of 59 mV and which suggest one electron redox phenomena. The third wave displayed a considerably larger amplitude and peak-to-peak separation (122 mV), suggesting a multielectron process. The two-electron wave of polymer **33** was resolved into two single electron waves in the CV of polymer **21** (Figure 5b), giving a total of four single-electron redox processes at 0.227, 0.475, 0.867, and 1.027 V. Janssen and co-workers have studied small molecule versions of these polymers, and they found a similar four-wave voltammogram for a meta,para *N*-phenylaniline tetramer.[20] They suggested that the first two waves arose from removal of a single electron from neighboring *p*-phenylenediamine units of the molecule, while the second set of waves resulted from oxidation of the second nitrogen in the para unit. It is probable that an analogous redox behavior is occurring in our polymeric samples (Scheme 3). The cyclic voltammogram for the alternating aminobiphenylene aniline polymer **15** with para regiochemistry (Figure 5c) was similar to those of **21** and **33**, but the individual waves within the two primary regimes were less well resolved.

Oxidation waves for the all meta polymer **28** (Figure 6a) were visible at 0.381 and 0.588 V before a destructive oxidation occurred at about 0.9 V; the corresponding reduction waves were less visible. The voltammogram was unchanged after repeated scans, indicating that the low intensity of the reduction peaks

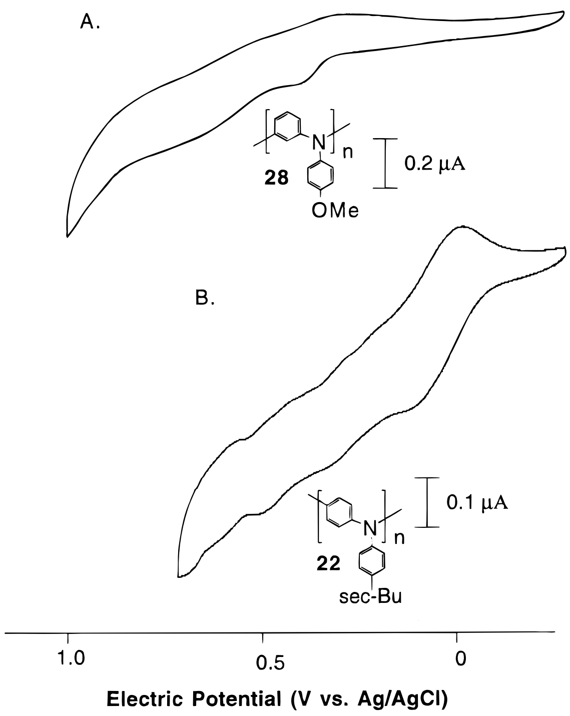
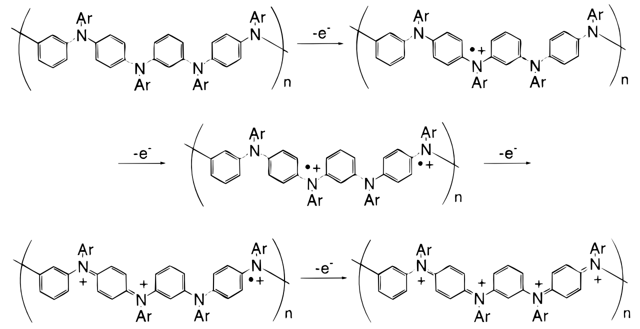


Figure 6. Cyclic voltammograms for (A) polymer **28** and (B) polymer **22**.

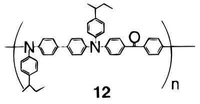
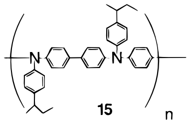
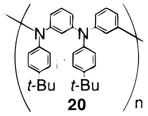
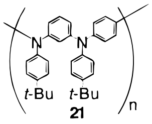
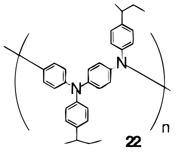
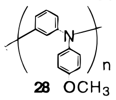
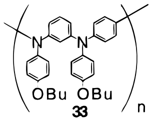
Scheme 3. Possible Oxidation States for Poly(*N*-arylaniline)s with Alternating Meta and Para Regiochemistry



is not due to oxidative decomposition of the sample. The shape of the cyclic voltammogram for polymer **20** with *tert*-butyl substituents on the *N*-aryl groups is similar to that of **28**, but the waves are shifted to 0.462 and 0.682 V. These data demonstrate the ability to tune the redox potential with the *N*-aryl substituent; replacement of the electron-rich methoxy side groups with the electron−neutral *tert*-butyl groups makes the polymer more difficult to oxidize.

The all-para polymer **22** (Figure 6b) exhibits a well-defined and chemically reversible redox wave at 0.030 V, with subsequent processes that are poorly defined. The large peak-to-peak width for the primary process suggests that multiple electrons may be involved and that the discrete oxidation states associated with the parent poly(*p*-aniline)[1] may not be present with this polymer. However, it should be noted that this material was considerably less soluble than the other polymers. Thus, we conducted voltametric analysis with low molecular weight samples ($M_n = 6500$, $M_w = 14000$, synthesized with a 40% excess of dibromobenzene monomer) to maintain homogeneous solutions. As a result, the broad peaks may be due to end-group effects that might result from the shorter chain lengths.

Table 7. UV−Vis and Thermal Characterization of Selected Polymers

Polymer	λ_{max} [a]	T_d [b]
	287	
	367	533
	307	428
	316	553
	333	485
	303	457
	315	

[a] Wavelength of maximum absorbance. [b] Temperature at which polymer decomposition begins (°C).

Cyclic voltammograms for the donor−acceptor polymers **12** and **19** are presented in Figure 7, parts a and b. Aminobiphenylene/benzophenone polymer **12** exhibited two well-resolved redox processes at 0.556 and 0.748 V. The narrow peak-to-peak distances (71 and 67 mV, respectively) for the two waves again suggested that these correspond to single-electron processes, which are most likely the first and second oxidation of the benzidene moieties. The *m*-phenylenediamine/benzophenone polymer **19** showed only a single oxidation wave at 0.681 V. As was the case with the *m*-poly(*N*-arylaniline) derivatives, the corresponding reduction wave was less pronounced. The absence of a second oxidation of **19** before the destructive oxidation of the polymer at 1.3 V suggests that the second nitrogen unit of the oxidized phenylenediamine ring is not readily oxidized.

UV−Visible Spectroscopy of Oxidized Polymers. The oxidation of polymers **15**, **28**, and **33** with bis(trifluoroacetoxy)-iodobenzene was monitored by UV−vis spectroscopy. A solution of polymer in dichloromethane that was 0.1 mM in repeat unit was treated repeatedly under nitrogen with ca. 0.1 equiv of a 0.01 M solution of bis(trifluoroacetoxy)iodobenzene in dichloromethane. The neutral polymers were colorless solutions that exhibited a single band in dichloromethane (Table 7). With the addition of oxidant, there was an incremental decrease in intensity of the absorption of the neutral polymer that was accompanied by the appearance and increase in intensity of two new bands attributed to the oxidized polymer. In addition, the color of the solutions turned a yellow-green color. As shown in Figure 8a, the para linked polymer **15** showed a decrease in the band at 367 nm and formation of bands

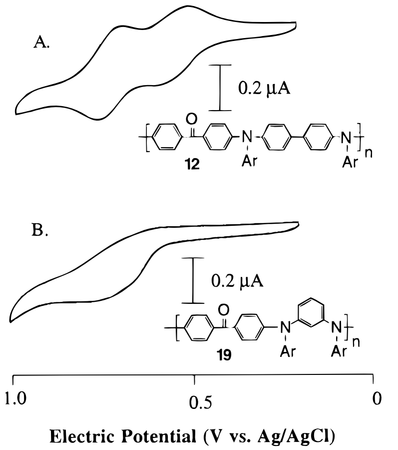


Figure 7. Cyclic voltammograms for (A) polymer **12** and (B) polymer **19**.

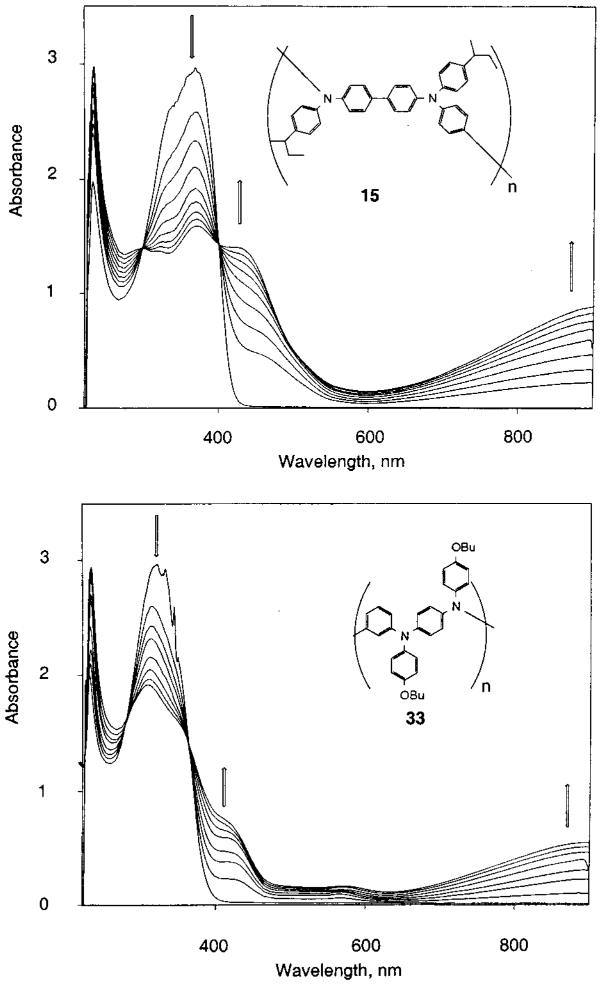


Figure 8. UV−vis spectra for oxidation of (A) polymer **15** and (B) polymer **33**.

at 450 and 900 nm along with isosbestic points at 298 and 400 nm. As shown in Figure 8b, the meta−para linked polymer **33** showed a decrease in the band at 315 nm and formation of bands at 430 and 900 nm, along with isosbestic points at 280 and 361 nm. Little additional oxidation was observed upon treatment of polymers **15** and **33** with increasing quantities of bis(trifluoroacetoxy)iodobenzene. In contrast to the clean oxidation of **33**, the all-meta linked polymer **28** showed no change in the UV−vis spectrum when oxidant was added to a 0.1 mM solution. However, when the oxidation was conducted at 0.9 mM a shoulder at 450 nm was observed.

These data indicate that the polymers formed from palladium-catalyzed amination reactions are clean enough to give straightforward oxidation behavior that is typical of triarylamine small molecules. Further, the observation of a band near 900 nm is similar to that of oxidized and protonated "leucoemeraldine" polyaniline, for which polymer **15** is an organic-soluble *N*-aryl analogue. Further, the observation of clean UV−vis spectra for the oxidation process with clear isosbestic points indicates that the radical cation form of the polymer is relatively stable at room temperature.

Magnetic Susceptibility Measurements and EPR. One might expect that oxidation of every nitrogen in the all-meta-linked polymer **28** and every other nitrogen in **33** would generate a system with ferromagnetic coupling of the spins as a result of their meta disposition at the phenyl ring. With clear evidence that bis(trifluoroacetoxy)iodobenzene does oxidize the triarylamine polymer containing alternating meta and para linkages, samples of **33** in CH_2Cl_2 were oxidized with 0.45 and 2.70 equiv/nitrogen atom of bis(trifluoroacetoxy)iodobenzene, and the magnetic susceptibility of the resulting samples was measured by the method of Evans.[54] Reaction of **33** with 0.9 and 5.4 equiv of oxidant per repeat unit led to NMR shifts that corresponded to gram susceptibilites of 2.1×10^{-6} and 2.3×10^{-6} cm^3/g, respectively. Janssen reported that this oxidant was only strong enough to remove electrons from the first set of oxidation waves (vide supra) in meta−para triarylamine oligomers,[20] and our UV−vis studies on **33** showed that additional oxidation with bis(trifluoroacetoxy)iodobenzene did not occur after adding 1 equiv of oxidant per monomer. Thus, the gram susceptibilities for the two samples of **33** generated with different quantities of oxidant were essentially identical. A substantial amount of the material remained oxidized at room temperature over the course of 24 h, but the magnetic susceptibility for oxidized **33** did decay to 1.2×10^{-6} after 2.5 h at room temperature and to 0.8×10^{-6} after 24 h. Janssen reported that the oxidized form of discrete oligomeric materials was stable for several weeks.[55] As one might expect from the UV−vis data above, oxidation of all meta-linked polymer **28** gave no detectable paramagnetic shift for an oxidized polymer when treated with bis(trifluoroacetoxy)iodobenzene.

Oxidized **33** also exhibited a very strong EPR signal at 70 K in CH_2Cl_2. The spectrum consisted of a single, featureless line centered at about 3300 G corresponding to a $\Delta M_s = \pm 1$ transition typical for spin = 1/2 organic radicals. We were unable to observe a $\Delta M_s = \pm 2$ transition in the $g = 4$ region that would have indicated higher spin states resulting from ferromagnetic coupling. However, other research in our group has found the observation of this transition in *N*-arylaniline oligomers to be solvent dependent; transitions in the $g = 4$ region that were not observed in CH_2Cl_2 were detected in butyronitrile solvent.[56] Unfortunately, polymer **33** was not soluble in butyronitrile. Further experiments to characterize the magnetic properties of these materials are currently in progress.

Thermal Characterization of Polymers. One goal for preparing these triarylamine polymers was to create an organic-soluble material that had the electrochemical properties of triarylamine small molecules and the thermal and physical properties of high molecular weight polymers. Samples of polymers were subjected to thermal gravimetric analysis (TGA).

---

(54) Evans, D. F. *J. Chem. Soc.* **1959**, 2003.

(55) Wienk, M. M.; Janssen, R. A. J. *J. Chem. Soc., Chem. Commun.* **1996**, 267.

(56) Louie, J. Ph.D. Dissertation Thesis, Yale University, 1998.

The polymers were found to be thermally stable with decomposition occurring at temperatures greater than 400 °C as shown in Table 7. Thus, the palladium-catalyzed amination chemistry does produce materials with reversible oxidation chemistry and high thermal stability. With the appropriate tuning of *N*-aryl side chains, amorphous polymers with high glass transition temperatures should be accessible.

Conclusions

We have shown that the use of phosphines such as **7** and **8** reduces side reactions which had previously limited the molecular weight and purity of triarylamine polymers produced from palladium-catalyzed chemistry. The strategies for eliminating these reactions are likely to be useful for other palladium-catalyzed polymerization processes, including the preparation of pure samples of diarylamine polymers. The use of an alkyl or simple methoxymethylarylphosphine eliminated aryl group exchanges and eliminated phosphine arylation that occurred with tri-*o*-tolylphosphine. Tri-*o*-tolylphosphine had been used previously in polymer chemistry because it does not undergo aryl group exchange. The use of ligands **7** and **8** substantially improved molecular weight and produced phosphine-free polymer samples, but additional strategies were necessary to overcome cyclization processes that competed with chain growth. Cyclization was minimized through the polymerization of “pentameric monomers”. In addition, cyclic impurities were removed by filtration of the sample through a Sephadex column. The materials were studied by cyclic voltammetry and showed a number of interesting features, including a demonstration that the redox potential can be tuned by varying the *N*-aryl side chain. The oxidized form of polymer **33** with alternating meta and para regiochemistry that was observed by UV−vis spectroscopy after oxidation with bis(trifluoroacetoxy)iodobenzene was shown to be paramagnetic by the Evans method and to exhibit a strong ESR signal. Overall, these polymers constitute thermally stable, organic soluble polymers with reversible oxidation chemistry involving radical cations that display good stability at room temperature in solution.

Experimental Section

General Methods. Schlenk-line or drybox techniques were used for all air-sensitive manipulations. ^{1}H NMR spectra were acquired at 500 MHz using a Bruker AM-series spectrometer. Proton-decoupled ^{13}C NMR spectra were similarly obtained at 125 MHz, while proton-decoupled ^{31}P NMR spectra were obtained at 202 MHz using a GE Omega 300 spectrometer. ^{1}H and ^{13}C chemical shifts are referenced to residual proton signals in the deuterated solvent; ^{31}P chemical shifts are reported relative to an external standard of 85% phosphoric acid. Toluene, THF, ether, benzene, and pentane solvents were distilled from sodium/benzophenone prior to use. Dichloromethane was distilled from calcium hydride prior to use. Bis[2-(trifluoromethyl)phenyl]monochlorophosphine,[57] *o*-(diphenylphosphino)methoxymethylbenzene (**5**),[46] 1-[2′-(diphenylphosphino)phenyl]methoxyethane (**6**),[47] and tris(*o*-methoxymethylphenyl)phosphine (**7**)[48] were prepared by literature procedures. 4,4′-Dibromobenzophenone (**10**), 1,4-dibromobenzene (**14**), 4,4′-dibrombiphenyl, diphenylamine, and ditolylamine were purchased from commercial suppliers and were sublimed under reduced pressure prior to use; 1,3-dibromobenzene (**17**) was similarly purchased and vacuum distilled from calcium hydride. Other chemicals were used as received from commercial suppliers. Cyclic voltammetry was carried out on a BAS CV-27 Voltammograph. A platinum and a Ag/AgCl electrode were used as working and reference electrodes, and the reported potentials were calibrated with an external sample of ferrocene. All runs were performed in 1 mM solutions in dry CH_2Cl_2 in the presence of Bu_4NPF_6. X-Band EPR measurements were conducted on 1 mM solutions on a Varian E9 spectrometer interfaced with a MacIntosh Computer. The UV−vis oxidations utilized a Perkin-Elmer Lambda 6 spectrophotometer. GPC chromatograms were recorded in THF solvent with a Waters HPLC system consisting of a 515 HPLC pump, 410 differential refractometer, Styrogel columns, and Millenium software. The listed values are relative to known standards of polystyrene. Mass spectrometry analyses were performed by the Mass Spectrometry Facility at the University of Illinois at Urbana−Champaign. Analytical data were obtained by Robertson Microlit Laboratories, Inc. All polymeric materials were subjected to elemental analysis. However, incomplete combustion of the materials led to large deviations in repeated analyses of the same sample and significant quantities of ash were produced in the combustion analyses. Thus, analyses are reported, along with the percentage of ash residue that was obtained.

Bis[2-(trifluoromethyl)phenyl]mono(2-methoxyphenyl)-phosphine (2). A solution of 0.667 g (1.67 mmol) of bis[2-(trifluoromethyl)phenyl]monochlorophosphine in dry THF was chilled to −78 °C under nitrogen in a 50 mL Schlenk flask. A Grignard solution prepared from 0.411 g (2.20 mmol) of 2-bromoanisole and 58.8 mg (2.40 mmol) of Mg was added dropwise via cannula. The flask was allowed to warm to room temperature, and then fitted with a reflux condenser. The reaction was then refluxed overnight, resulting in a deep reddish-brown solution. The solvent was removed in vacuo, and the residue was extracted with ether and rinsed with brine. After the organic phase was dried ($MgSO_4$), the solvent was removed with a rotary evaporator. The residue was then chromatographed on silica with 5% EtOAc in hexanes. The material from chromatography was then recrystallized in the drybox from THF/pentane, resulting in the isolation of 0.255 g (0.596 mmol, 35.7%) of **2** as a white solid: ^{1}H NMR (C_6D_6) δ 3.05 (s, 3H), 6.40 (m, 1H), 6.68 (m, 2H), 6.86 (m, 4H), 7.05 (br, 1H), 7.15 (br, 2H), 7.47 (m, 2H); ^{13}C NMR (C_6D_6) δ 55.3, 110.7, 121.5, 125.0 (q, $J = 275$ Hz), 125.1 (br), 126.8 (q, $J = 5.4$ Hz), 129.0, 130.9, 131.4, 134.3, 135.1 (br), 136.1, 136.6 (d, $J = 31.6$ Hz), 161.3 (d, $J = 16.8$ Hz); ^{31}P NMR (C_6D_6) δ −28.2 (complex heptet). Anal. Calcd for $C_{21}H_{15}F_6OP$: C, 58.89; H, 3.53. Found: C, 58.78; H, 3.54.

Bis(2-methoxyphenyl)mono[2-(trifluoromethyl)phenyl]-phosphine (3). A 100 mL Schlenk flask charged with 2.02 g (14.7 mmol) of PCl_3, 30 mL of dry THF, and a stirbar was chilled to −78 °C under nitrogen. A Grignard solution made from 3.30 g (14.7 mmol) of 2-bromobenzotrifluoride and 0.388 g of Mg (1.1 equiv) was added dropwise from an addition funnel. The reaction was warmed to room temperature and allowed to stir for 5 h. The solvent was removed in vacuo and 50 mL of fresh THF was added. The solution was then chilled to −78 °C, and a second Grignard reagent synthesized from 5.50 g (29.4 mmol) 2-bromoanisole and 0.846 g (35.3 mmol) of Mg was added dropwise via cannula. The reaction was allowed to warm to room temperature, and the flask was fitted with a reflux condenser. After the solution was heated at reflux overnight, the reaction was quenched with 2 mL of methanol, and the solvent was removed in vacuo. The residue was dissolved in ethyl acetate, rinsed with brine, and dried over $MgSO_4$. After removal of the solvent, the crude product was suspended in cold ether and filtered. It was then recrystallized from degassed ethanol/ethyl acetate until colorless to yield 2.25 g (5.76 mmol, 39.2%) of **3** as a white solid: ^{1}H NMR (C_6D_6) δ 3.14 (s, 6H), 6.46 (dd, $J = 7.8$ Hz, 6.0 Hz, 2H), 6.74 (t, $J = 7.2$ Hz, 2H), 6.86 (m, 2H), 6.94 (br, 2H), 7.09 (t, $J = 7.5$ Hz, 2H), 7.34 (m, 1H), 7.54 (m, 1H); ^{13}C NMR (C_6D_6) δ 55.2, 110.6, 121.2, 125.4 (q, $J = 273$ Hz), 125.7 (d, $J = 17.5$ Hz), 126.3 (m), 128.7, 130.4, 131.4, 134.0, 135.4 (m), 136.7, 138.1 (d, $J = 31.1$ Hz), 161.6 (d, $J = 16.5$ Hz); ^{31}P NMR (C_6D_6) δ −29.1 (q, $J = 95.3$ Hz). Anal. Calcd for $C_{21}H_{18}F_3OP$: C, 64.62; H, 4.65. Found: C, 64.52; H, 4.60.

Model Amination Reactions on Small Molecules. A reactant stock solution that was 0.1 M in aryl halide, 0.1 M in diarylamine, and 0.09 M in 1,3,5-trimethoxybenzene was prepared in a drybox in dry C_6D_6. A catalyst stock solution which was 2.0 mM in $Pd(OAc)_2$ was prepared similarly. In the drybox, 6.0 μmol samples of the various phosphines were weighed into separate vials, along with 14.4 mg (0.150 mmol) of sodium *tert*-butoxide. Each vial was then charged with 1.0 mL of the reactant stock (0.10 mmol of reactants), 1.0 mL of the catalyst stock

---

(57) Sihler, R.; Werz, U.; Brune, H.-A. *J. Organomet. Chem.* **1989**, *368*, 213.

(2.0 μmol of Pd), and a stirbar. The vials were then sealed with a Teflon-lined screw-cap, removed from the drybox, and heated in a 90 °C oil bath. Reactions between di(*p*-tolyl)amine and 4-bromobenzophenone were heated for 24 h, while the reactions between diphenylamine and 4-bromo-*N*,*N*-dimethylaminobenzene were allowed to proceed for 48 h. Aliquots were then removed from the vials and placed into 5 mm NMR tubes. The yields were determined by integrating the resonances for the methyl protons vs the 1,3,5-trimethoxybenzene internal standard. The results for these experiments are presented in Tables 1 and 3.

4-(*N*,*N*-Di(*p*-tolyl)amino)benzophenone (9). In a drybox, a 5 mL screw-capped test tube was charged with 117.5 mg (0.450 mmol) of 4-bromobenzophenone, 88.9 mg (0.450 mmol) of di(*p*-tolyl)amine, 64.8 mg (0.675 mmol) of sodium *tert*-butoxide, 2.0 mg (9.0 μmol) of Pd(OAc)$_2$, 5.5 mg (27 μmol) of tri(*tert*-butyl)phosphine, 3 mL of benzene, and a stirbar. The tube was sealed with a Teflon-lined screw cap, removed from the drybox, and heated in a 90 °C oil bath for 18 h. The reaction was then rinsed with saturated NH$_4$Cl (2 mL), and the resulting aqueous phase was washed twice with 1 mL of ether. The organic layers were combined and dried over MgSO$_4$. Removal of the solvent with a rotary evaporator followed by chromatography on silica (10% EtOAc in hexanes) resulted in a bright yellow oil. This oil was heated in a Kugelrohr oven at 60 °C under a dynamic 5 mTorr vacuum for 2 h to yield 163.4 mg (0.433 mmol, 96.3%) of **9** as a yellow, glassy resin which fluoresced strongly in the green under ambient light: ^{1}H NMR (CDCl$_3$) δ 2.34 (s, 6H), 6.79 (dt, $J = 8.9$ Hz, 2.5 Hz, 2H), 7.08 (d, $J = 8.4$ Hz, 4H), 7.14 (d, $J = 8.4$ Hz, 4H), 7.45 (t, $J = 7.7$ Hz, 2H), 7.53 (tt, $J = 7.4$ Hz, 1.3 Hz, 1H), 7.68 (dt, $J_d = 8.9$ Hz, $J_t = 2.5$ Hz, 2H), 7.76 (d, $J = 6.9$ Hz, 2H); ^{13}C NMR (CDCl$_3$) δ 20.9, 118.3, 126.1, 128.1, 128.6, 129.6, 130.2, 131.5, 132.0, 134.5, 138.7, 143.9, 152.3, 195.1. Anal. Calcd for $C_{27}H_{23}NO$: C, 85.91; H, 6.14; N, 3.71. Found: C, 86.03; H, 6.06; N, 3.71.

[4-(*N*′,*N*′-Dimethylamino)phenyl]diphenylamine (13). A procedure identical with that for the isolation of **9** was followed utilizing 90.0 mg (0.450 mmol) of 4-bromo-*N*,*N*-dimethylaminobenzene and 76.1 mg (0.450 mmol) of diphenylamine. Chromatography with 5% EtOAc in hexanes resulted in the isolation of 114.1 mg (0.396 mmol, 88.0%) of **13** as a white crystalline solid: ^{1}H NMR (C$_6$D$_6$) δ 2.47 (s, 6H), 6.49 (dt, $J = 9.0$ Hz, 2.0 Hz, 2H), 6.81 (t, $J = 7.5$ Hz, 2H), 7.07 (t, $J = 7.4$ Hz, 4H), 7.10 (d, $J = 9.0$ Hz, 2H), 7.18 (d, $J = 7.5$ Hz, 4H); ^{13}C NMR (C$_6$D$_6$) δ 40.5, 114.1, 121.7, 123.0, 128.2, 129.3, 137.7, 148.1, 149.0. Anal. Calcd for $C_{20}H_{20}N_2$: C, 83.30; H, 6.99; N, 9.71. Found: C, 83.09; H, 6.84; N, 9.64.

Bisamine Monomer Synthesis, General Procedure. In a drybox, 15.0 mmol of dibromide, 45.0 mmol of substituted aniline, 169 mg (0.750 mmol, 2.5%) of palladium acetate, 0.830 g (1.50 mmol) of bis(diphenylphosphino)ferrocene, and 4.30 g (45.0 mmol) of sodium *tert*-butoxide were weighed directly into a 50 mL screw-capped test tube. A stirbar was added along with 40 mL of toluene. The tube was then sealed with a cap, removed from the drybox, and heated in a 90 °C oil bath for 12 h. The reaction product was isolated as described below for each compound.

***N*,*N*′-Di(4-*sec*-butylphenyl)-4,4′-diaminobiphenyl (11).** The above general procedure was followed using 4.68 g (15.0 mmol) of 1,4-dibromobiphenyl and 6.71 g (15.0 mmol) of 4-*sec*-butylaniline in 40 mL of toluene. The crude reaction was treated with 100 mL of 0.5 M citric acid and extracted 3 times into 100 mL of chloroform. The organic phases were then combined and dried over MgSO$_4$. The solvent was evaporated under reduced pressure. Silica gel chromatography of the resulting material, eluting with 10% ethyl acetate in hexanes, gave a yellow solid. This solid was washed with cold 10% ethyl acetate in hexanes to remove colored impurities, and the resulting material was recrystallized from degassed hexanes/ethyl acetate to yield 5.33 g (11.9 mmol, 79.3% yield) of **11** as white crystals: ^{1}H NMR (500 MHz, C$_6$D$_6$) δ 0.84 (t, $J = 7.3$ Hz, 6H), 1.20 (d, $J = 7.0$ Hz, 6H), 1.53 (m, 4H), 2.45 (m, 2H), 5.09 (s, 2H), 6.93 (dd, $J = 8.4$ Hz, 1.6 Hz, 8H), 7.02 (d, $J = 8.4$ Hz, 4H), 7.45 (d, $J = 8.5$ Hz, 4H); ^{13}C NMR (125 MHz, C$_6$D$_6$) δ 12.5, 22.3, 31.6, 41.4, 118.0, 118.9, 127.6, 128.1, 133.7, 140.5, 141.4, 142.9. Anal. Calcd for $C_{32}H_{36}N_2$: C, 85.67; H, 8.09; N, 6.24. Found: C, 85.59; H, 7.95; N, 6.15.

***N*,*N*′-Di(4-*tert*-butylphenyl)-1,3-phenylenediamine (16).** The above general procedure was followed using 3.54 g (15.00 mmol) of 1,3-dibromobenzene and 6.70 g (45.0 mmol) of 4-*tert*-butylaniline. The crude reaction was treated with 20 mL of 2% HCl and extracted 3 times into 30 mL of diethyl ether. The organic phases were then combined and dried over MgSO$_4$. The solvent was removed under reduced pressure, and the resulting material was chromatographed on silica gel eluting with 5% ethyl acetate in hexanes. The resulting solid was recrystallized from hexanes/ethyl acetate to yield 4.30 g (11.5 mmol, 76.7% yield) of **16** as colorless needles: ^{1}H NMR (500 MHz, C$_6$D$_6$) δ 1.25 (s, 18H), 5.00 (s, 2H), 6.52 (dd, $J = 8.0$, 2.0 Hz, 2H), 6.59 (m, 1H), 6.94 (dd, $J = 6.6$, 2.0 Hz, 4H), 7.06 (t, $J = 8.0$ Hz, 1H), 7.21 (dd, $J = 6.6$, 2.0 Hz, 4H); ^{13}C NMR (125 MHz, C$_6$D$_6$) δ 31.6, 34.2, 105.5, 109.5, 119.3, 126.3, 130.3, 140.9, 144.1, 145.6. Anal. Calcd for $C_{26}H_{32}N_2$: C, 83.82; H, 8.66; N, 7.52. Found: C, 83.92; H, 8.66; N, 7.52.

***N*,*N*′-Di(4-*sec*-butylphenyl)-1,4-phenylenediamine (18).** The above general procedure was followed using 0.707 g (3.00 mmol) of 1,4-dibromobenzene and 1.34 g (9.00 mmol) of 4-*sec*-butylaniline. The crude reaction was treated with 20 mL of 2% HCl and extracted three times into 30 mL of diethyl ether. The organic phases were then combined and dried over MgSO$_4$. The solvent was removed under reduced pressure and the resulting material was chromatographed on silica gel eluting with 10% ethyl acetate in hexanes. The resulting solid was taken into a drybox and recrystallized from air-free ether and pentane to give 0.635 g (1.70 mmol, 56.7% yield) of **18** as white, flaky crystals: ^{1}H NMR (500 MHz, C$_6$D$_6$) δ 0.84 (t, $J = 7.5$ Hz, 6H), 1.20 (d, $J = 6.5$ Hz, 6H), 1.53 (m, 4H), 2.44 (m, 2H), 4.90 (s, 2H), 6.85 (s, 4H), 6.86 (d, $J = 7.5$ Hz, 4H), 7.05 (d, $J = 7.5$ Hz, 4H); ^{13}C NMR (125 MHz, C$_6$D$_6$) δ 12.5, 22.4, 31.6, 41.3, 117.3, 120.6, 128.5, 137.9, 139.3, 142.9. Anal. Calcd for $C_{26}H_{32}N_2$: C, 83.82; H, 8.66; N, 7.52. Found: C, 83.63; H, 8.73; N, 7.43.

***N*,*N*′-Di(4-methoxyphenyl)-1,3-phenylenediamine (23).** The above general procedure was followed using 14.2 g (60.0 mmol) of 1,3-dibromobenzene, 22.2 g (180 mmol) of *p*-anisidine, and 100 mL of toluene in a 200 mL Schlenk flask. The crude reaction was treated with 100 mL of 0.5 M citric acid and extracted three times with 100 mL of chloroform. The organic phases were then combined and dried over MgSO$_4$. The solvent was evaporated under reduced pressure. The resulting solid was washed with 30% ethyl acetate in hexanes and recrystallized from hexanes/ethyl acetate to yield 14.0 g (43.8 mmol, 73.0% yield) of **23** as pale purplish needles: ^{1}H NMR (500 MHz, C$_6$D$_6$) δ 3.32 (s, 6H), 4.83 (s, 2H), 6.39 (m, 3H), 6.74 (m, 4H), 6.91 (m, 4H), 7.06 (t, $J = 8.1$ Hz, 1H); ^{13}C NMR (125 MHz, C$_6$D$_6$) δ 55.0, 103.2, 107.6, 114.8, 122.8, 130.3, 136.3, 146.8, 155.8. Anal. Calcd for $C_{20}H_{20}N_2O_2$: C, 74.98; H, 6.29; N, 8.74. Found: C, 74.77; H, 6.37; N, 8.96.

***N*,*N*′-Di(4-*n*-butoxyphenyl)-1,3-phenylenediamine (29).** The above general procedure was followed using 0.707 g (3.00 mmol) of 1,3-dibromobenzene and 1.98 g (9.00 mmol) of 4-*n*-butoxyaniline. The crude reaction was treated with 20 mL of 0.5 M citric acid and extracted three times with 30 mL of diethyl ether. The organic phases were then combined and dried over MgSO$_4$. The solvent was removed under reduced pressure and the resulting material was chromatographed on silica gel eluting with 10% ethyl acetate in hexanes. The resulting solid was recrystallized from hexanes/ethyl acetate to yield 0.942 g (2.33 mmol, 77.6% yield) of **29** as colorless needles: ^{1}H NMR (500 MHz, C$_6$D$_6$) δ 0.83 (t, $J = 7.5$ Hz, 6H), 1.34 (m, 4H), 1.57 (m, 4H), 3.64 (t, $J = 6.5$ Hz, 4H), 4.86 (s, 2H), 6.41 (m, 3H), 6.80 (d, $J = 9.0$ Hz, 4H), 6.93 (d, $J = 8.8$ Hz, 4H), 7.07 (t, $J = 7.9$ Hz, 1H); ^{13}C NMR (125 MHz, C$_6$D$_6$) δ 13.9, 19.5, 31.7, 67.9, 103.2, 107.6, 115.5, 122.9, 130.3, 136.2, 146.9, 155.4. Anal. Calcd for $C_{26}H_{32}N_2O_2$: C, 77.19; H, 7.97; N, 6.92. Found: C, 77.18; H, 8.01; N, 6.81.

General Polymerization Procedure. In a drybox, 0.250 mmol of bisamine and dihalide were weighed into a 1 dram screw-capped vial along with 72 mg (0.75 mmol) of sodium *tert*-butoxide, a stirbar, and 0.250 mL (0.5 mol %) of a stock solution that is 0.01 mM in Pd(OAc)$_2$ and 0.03 mM in tri(*tert*-butyl)phosphine (**8**). The vial was sealed with a Teflon-lined serum cap, removed from the drybox, and placed in a 90 °C oil bath. The mixture became fluid within a few minutes, and then formed a gel soon afterward. The reaction was heated for an additional 3 days to ensure complete reaction. After treatment with 2 mL of 0.5 M citric acid, the crude polymer was extracted three times into 2 mL of the workup solvent (see below for specific procedures). Stirring and application of heat and sonication was often necessary at this stage to completely dissolve the polymer. The organic layers were combined and the resulting polymer solution was then extracted with 5% KCN to remove residual catalyst. After drying over MgSO$_4$, removal of the solvent resulted in a film, which was dissolved in a minimum amount of workup solvent. The polymer product was then precipitated by transferring the solution into 50 mL of methanol by pipet. The solid was isolated via filtration or centrifugation, rinsed with water, methanol, and hexanes, and then dried in vacuo. For yields and variations on the conditions, see Tables 2 and 4−6.

Polymerization of 10 with 11. Using the general procedure, polymer **12** was extracted with chloroform and isolated via filtration to yield **12** as a yellow-orange filmy solid: ^{1}H NMR (500 MHz, CDCl$_3$) δ 0.86 (t, $J = 7.2$ Hz, 6H), 1.25 (d, $J = 6.7$ Hz, 6H), 1.60 (m, 4H), 2.60 (m, 2H), 7.05 (d, $J = 8.3$ Hz, 4H), 7.11 (d, $J = 8.3$ Hz, 4H), 7.14 (d, $J = 8.2$ Hz, 4H), 7.20 (d, $J = 8.0$ Hz, 4H), 7.50 (d, $J = 8.1$ Hz, 4H), 7.70 (d, $J = 8.2$ Hz, 4H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 12.3, 21.7, 31.2, 41.1, 119.7, 125.4, 126.0, 127.6, 128.2, 130.4, 131.6, 135.9, 144.0, 145.8, 151.4, 193.8. Anal. Calcd for C$_{42}$H$_{42}$N$_4$O: C, 86.22; H, 6.75; N, 4.46. Found: C, 83.90; H, 6.68; N, 4.08; Ash, 0.50.

Polymerization of 11 with 14. Using the general procedure, the polymer was extracted with toluene and isolated via filtration to yield **15** as an off-white filmy solid: ^{1}H NMR (500 MHz, CDCl$_3$) δ 0.86 (t, $J = 7.1$ Hz, 6H), 1.24 (d, $J = 6.5$ Hz, 6H), 1.58 (m, 4H), 2.56 (m, 2H), 7.02 (s, 4H), 7.08 (s, 8H), 7.12 (d, $J = 7.9$ Hz, 4H), 7.43 (d, $J = 7.5$ Hz, 4H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 12.3, 21.7, 31.2, 41.0, 123.0, 124.3, 125.1, 127.0, 127.7, 134.0, 142.3, 142.7, 145.3, 146.8. Anal. Calcd for C$_{38}$H$_{38}$N$_2$: C, 87.31; H, 7.33; N, 5.36. Found: C, 85.24; H, 7.30; N, 4.91; Ash, 1.08.

Polymerization of 10 with 16. Using the general procedure, the polymer was extracted with chloroform and isolated via filtration to yield **19** as a bright yellow filmy solid. Removal of the majority of cyclic impurities was achieved by filtration of 150 mg through a 12 in. × 1.5 in. column of Sephadex LH-60 SEC resin using THF as eluent. The resulting polymer was isolated as before (70.9% recovery) and extracted with hexanes using a Soxhlet apparatus for 3 h to remove BHT and other impurities from the product: ^{1}H NMR (500 MHz, CDCl$_3$) δ 1.29 (s, 18H), 6.84 (d, $J = 7.6$ Hz, 2H), 6.99 (d, $J = 8.3$ Hz, 4H), 7.06 (d, $J = 8.3$ Hz, 4H), 7.19 (br, 2H), 7.29 (d, $J = 8.3$ Hz, 4H), 7.643 (d, $J = 8.3$ Hz, 4H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 31.4, 34.4, 119.7, 120.8, 122.1, 125.4, 126.4, 128.6, 130.4, 131.4, 143.5, 147.6, 147.7, 151.0, 193.6. Anal. Calcd for C$_{39}$H$_{38}$N$_2$O: C, 85.05; H, 6.95; N, 5.08. Found: C, 82.74; H, 6.72; N, 4.68; Br, <0.05; Ash, 1.18.

Polymerization of 16 with 17. Using the general procedure, the polymer was extracted with toluene and isolated via filtration to yield **20** as an off-white filmy solid. Removal of the majority of cyclic impurities was achieved by filtration of 70 mg through a 12 in. × 1.5 in. column of Sephadex LH-60 SEC resin using THF as eluent. The resulting polymer was isolated as before (73.2% recovery) and extracted with hexanes with a Soxhlet apparatus for 3 h to remove BHT and other impurities from the product: ^{1}H NMR (500 MHz, CDCl$_3$) δ 1.21 (s, 9H), 6.59 (dd, $J_d = 8.0$ Hz, $J_d = 1.8$ Hz, 2H), 6.78 (s, 1H), 6.85 (d, $J = 8.6$ Hz, 2H), 6.98 (t, $J = 8.0$ Hz, 1H), 7.09 (d, $J = 9.0$ Hz, 2H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 31.4, 34.1, 118.3, 119.8, 123.0, 125.7, 144.5, 145.0, 148.3. Anal. Calcd for C$_{16}$H$_{17}$N$_2$: C, 86.05; H, 7.67; N, 6.27. Found: C, 85.43; H, 7.64; N, 6.10; Ash, 0.51.

Polymerization of 14 with 16. Using the general procedure, the polymer was extracted with toluene and isolated via filtration to yield **21** as an off-white filmy solid. Removal of the majority of cyclic impurities could be achieved by filtration of 70 mg through a 12 in. × 1.5 in. column of Sephadex LH-60 SEC resin (with THF as eluent). The resulting polymer was isolated as before (66.3% recovery) and extracted with hexanes using a Soxhlet apparatus for 3 h to remove BHT and other impurities from the product: ^{1}H NMR (500 MHz, CDCl$_3$) δ 1.25 (s, 18H), 6.56 (dd, $J = 8.0$ Hz, 2.0 Hz, 2H), 6.87 (s, 1H), 6.90 (s, 4H), 6.95 (d, $J = 9.0$ Hz, 4H), 6.99 (t, $J = 8.0$ Hz, 1H), 7.17 (d, $J = 9.0$ Hz, 2H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 31.5, 34.2, 117.2, 118.2, 123.3, 125.1, 125.8, 129.5, 142.5, 144.8, 145.1, 148.5. Anal. Calcd for C$_{32}$H$_{34}$N$_4$: C, 86.05; H, 7.67; N, 6.27. Found: C, 85.21; H, 7.37; N, 6.35.

Polymerization of 14 with 18. Using the general procedure, the polymer was extracted with toluene and isolated via filtration to yield **22** as an off-white filmy solid. Very little cyclic oligomer was formed during this polymerization: ^{1}H NMR (500 MHz, CDCl$_3$) δ 0.835 (t, $J = 7.3$ Hz, 3H), 1.22 (d, $J = 6.8$ Hz, 3H), 1.57 (br m, 2H), 2.54 (br m, 1H), 6.95 (br s, 4H), 7.04 (br s, 4H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 12.3, 21.7, 31.2, 40.9, 122.9 (br), 124.6, 127.6, 141.6 (br), 142.6 (br), 145.6 (br). Anal. Calcd for C$_{16}$H$_{17}$N: C, 86.06; H, 7.67; N, 6.27. Found: C, 84.28; H, 7.54; N, 5.59; Ash, 2.08.

Dibromotrimer (24). In a drybox, 1.28 g (4.00 mmol) of **23**, 1.16 g (12.1 mmol) of sodium *tert*-butoxide, 177.2 mg (0.320 mmol) of bis(diphenylphosphino)ferrocene, 36.0 mg (0.160 mmol) of Pd(OAc)$_2$, and 50 mL of 1,3-dibromobenzene were combined in a 100 mL Schlenk flask along with a stirbar. The flask was removed from the drybox, placed under nitrogen, and heated in a 100 °C oil bath for 24 h to form a red-brown suspension. The resulting solution was then treated with water, and the layers were separated. The aqueous phase was rinsed twice with 20 mL of chloroform. The organic layers were combined and dried over MgSO$_4$. Evaporation of the chloroform was followed by removal of the excess dibromobenzene by distillation in a Kugelrohr apparatus (50 °C, 5 mTorr vacuum). The residue was then chromatographed on silica eluting with 5% ethyl acetate in hexanes. A slightly brownish resin was obtained, which was heated in a Kugelrohr oven overnight at 50 °C under a 5 mTorr vacuum to remove residual solvent and provide 1.95 g (3.10 mmol, 77.5%) of **24** as a brownish resin: ^{1}H NMR (500 MHz, C$_6$D$_6$) δ 3.25 (s, 6H), 6.62−6.63 (multiple resonances, 6H), 6.70 (t, $J = 8.0$ Hz, 2H), 6.84−6.90 (multiple resonances, 9H), 6.99 (s, 1H), 7.34 (s, 2H); ^{13}C NMR (125 MHz, C$_6$D$_6$) δ 54.9, 115.4, 118.0, 118.6, 120.7, 123.3, 124.6, 124.9, 128.1, 130.5, 130.6, 139.8, 148.7, 149.8, 157.3. Anal. Calcd for C$_{32}$H$_{26}$Br$_2$N$_2$O$_2$: C, 60.97; H, 4.16; N, 4.44. Found: C, 61.05; H, 4.29; N, 4.21.

Diaminotrimer (25). In a drybox, 1.79 g (2.83 mmol) of **24**, 1.26 g (10.2 mmol) of *p*-anisidine, 1.02 g (10.6 mmol) of sodium *tert*-butoxide, 152.5 mg (0.275 mmol) of bis(diphenylphosphino)ferrocene, 30.5 mg (0.135 mmol) of Pd(OAc)$_2$, and 10 mL of toluene were combined in a 50 mL sealable reaction tube along with a stirbar. The tube was removed from the drybox and heated in a 100 °C oil bath for 24 h to form a red-brown suspension. The suspension was then extracted with 2% HCl (2 × 10 mL) followed by saturated NaHCO$_3$ (2 × 10 mL). The aqueous phases were then rinsed twice with 10 mL of ether. The organic layers were combined and dried over MgSO$_4$. Evaporation of the solvent was followed by chromatography on silica with 20% ethyl acetate in hexanes to yield a slightly brownish resin. The resin was heated in a Kugelrohr oven overnight at 50 °C under a 5 mTorr vacuum to remove residual solvent, resulting in the isolation of 1.80 g (2.52 mmol, 89.1%) of **25** as a brownish resin: ^{1}H NMR (500 MHz, C$_6$D$_6$) δ 3.26 (s, 6H), 3.31 (s, 6H), 4.81 (s, 2H), 6.53 (dd, $J = 8.0$ Hz, 2.1 Hz, 2H), 6.66−6.71 (multiple resonances, 12H), 6.82 (dd, $J = 8.0$ Hz, 2.1 Hz, 2H), 6.87 (d, $J = 8.5$ Hz, 4H), 6.96−7.02 (multiple resonances, 3H), 7.12 (d, $J = 8.9$ Hz, 4H), 7.29 (t, $J = 2.1$ Hz, 1H); ^{13}C NMR (125 MHz, C$_6$D$_6$) δ 54.9, 55.0, 109.2, 111.2, 114.7, 114.8, 115.1, 117.1, 118.4, 122.3, 128.3, 130.0, 130.1, 136.0, 141.1, 146.4, 149.5, 149.6, 155.7, 156.7. Anal. Calcd for C$_{46}$H$_{42}$N$_4$O$_4$: C, 77.29; H, 5.92; N, 7.84. Found: C, 77.20; H, 6.04; N, 7.54.

Dibromopentamer (26). A procedure analogous to that for the preparation of **24** was employed using 1.76 g (2.46 mmol) of **25**, 0.713 g (7.43 mmol) of sodium *tert*-butoxide, 109 mg (0.196 mmol) of bis(diphenylphosphino)ferrocene, 22.1 mg (0.0984 mmol) of Pd(OAc)$_2$, and 30 mL of 1,3-dibromobenzene in a 50 mL sealable reaction tube. The crude product was chromatographed on silica with a gradient of 10−15% EtOAc in hexanes to yield an orange solid. This solid was recrystallized in cold ether to yield 2.01 g (1.96 mmol, 79.7% yield) of **26** as a beige powder: ^{1}H NMR (500 MHz, C$_6$D$_6$) δ 3.23 (s, 6H), 3.26 (s, 6H), 6.57−6.66 (multiple resonances, 10H), 6.77 (dm, $J_d = 6.0$ Hz, 4H), 6.83 (dm, $J_d = 8.5$ Hz, 2H), 6.87−6.92 (multiple resonances, 8H), 6.97 (d, $J = 9.0$ Hz, 4H), 7.01 (t, $J = 8.2$ Hz, 2H), 7.05 (t, $J = 2.1$ Hz, 2H), 7.09 (t, $J = 2.0$ Hz, 1H), 7.12 (t, $J = 7.6$ Hz, 1H), 7.34 (t, $J = 2.0$ Hz, 2H); ^{13}C NMR (125 MHz, C$_6$D$_6$) δ 54.9, 115.1, 115.2, 117.4, 118.3, 118.6, 120.4, 123.2, 124.3, 124.6, 125.6, 127.5, 128.5, 129.3, 130.1, 130.2, 130.5, 140.0, 140.5, 148.5, 149.1, 149.3, 150.0, 156.7, 157.1. Anal. Calcd for $C_{58}H_{48}Br_2N_4O_4$: C, 67.97; H, 4.72; N, 5.47. Found: C, 68.18; H, 5.06; N, 5.21.

Diaminopentamer (27). A procedure analogous to that for the preparation of **25** was employed using 0.800 g (0.780 mmol) of **26**, 0.288 g (2.34 mmol) of *p*-anisidine, 0.334 g (3.50 mmol) of sodium *tert*-butoxide, 50.0 mg (0.0903 mmol) of bis(diphenylphosphino)-ferrocene, 10.0 mg (0.044 mmol) of $Pd(OAc)_2$, and 3.5 mL of toluene. Chromatography of the crude product on silica with 25% EtOAc in hexanes resulted in a slightly brownish resin, which was heated in a Kugelrohr oven overnight at 50 °C under a 5 mTorr vacuum to remove residual solvent, yielding 0.769 g (0.692 mmol, 88.8%) of **27** as a brownish resin: ^1H NMR (500 MHz, C_6D_6) δ 3.23 (s, 6H), 3.25 (s, 6H), 3.31 (s, 6H), 4.78 (s, 2H), 6.53 (dd, $J = 8.0$ Hz, 1.6 Hz, 2H), 6.59−6.71 (multiple resonances, 16H), 6.76−6.79 (multiple resonances, 6H), 6.86 (d, $J = 8.9$ Hz, 4H), 6.93−6.99 (multiple resonances, 6H), 7.01 (d, $J = 8.9$ Hz, 4H), 7.08 (d, $J = 8.9$ Hz, 4H), 7.18 (t, $J = 2.1$ Hz, 2H); ^{13}C NMR (125 MHz, C_6D_6) δ 54.8, 54.9, 55.0, 109.2, 111.2, 114.8, 114.9, 115.0, 115.1, 116.9, 117.0, 117.1, 118.1, 118.3, 122.2, 127.4, 127.7, 129.9, 130.0, 130.1, 136.0, 140.8, 141.1, 146.3, 149.2, 149.3, 149.5, 149.6, 155.6, 156.5, 156.6. Anal. Calcd for $C_{72}H_{64}N_6O_6$: C, 77.96; H, 5.89; N, 7.58. Found: C, 77.71; H,5.67; N, 7.45.

Polymerization of 26 with 27. In a drybox, a 1 dram vial was charged with 51.2 mg (0.0500 mmol) of **26**, 55.5 mg (0.0500 mmol) of **27**, 14.4 mg (0.150 mmol) of sodium *tert*-butoxide, 50 μL of a benzene stock solution 0.01 mM in $Pd(OAc)_2$ and 0.03 mM in **8**, an additional 50 μL of benzene, and a stirbar. The vial was sealed with a Teflon-lined serum cap, removed from the drybox, and placed in a 90 °C oil bath for 3 days. Using the general procedure, the polymer was extracted into toluene. 63.0 mg (0.0400 mmol, 80.0% yield) of polymer **28** was isolated as a white filmy solid: ^1H NMR (500 MHz, $CDCl_3$) δ 3.67 (s, 3H), 6.49 (d, $J = 7.5$ Hz, 2H), 6.67−6.70 (multiple resonances, 3H), 6.89−6.94 (multiple resonances, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 55.3, 114.5, 116.6, 117.6, 126.7, 129.3, 140.4, 148.5, 155.8. Anal. Calcd for $C_{13}H_{11}NO$: C, 79.17; H, 5.62; N, 7.10. Found: C, 77.84; H, 5.56; N, 6.82; Ash, 1.69.

Dibromotrimer (30). In a drybox, 0.809 g (2.00 mmol) of **29**, 0.580 g (6.05 mmol) of sodium *tert*-butoxide, 88.6 mg (0.160 mmol) of bis(diphenylphosphino)ferrocene, 18.0 mg (0.080 mmol) of $Pd(OAc)_2$, 50 g of 1,4-dibromobenzene, and 5 mL of toluene were combined in a 50 mL sealable reaction tube. The reaction was removed from the drybox and heated in a 100 °C oil bath for 24 h to form a red-brown suspension. This suspension was then poured while hot into 150 mL of toluene and extracted with saturated NH_4Cl. The aqueous phase was rinsed twice with 20 mL of ether. The organic layers were combined and dried over $MgSO_4$. Evaporation of the solvent was followed by removal of the excess dibromobenzene by distillation in a Kugelrohr apparatus (50 °C, 5 mTorr). The residue was then chromatographed on silica with 1% ethyl acetate in hexanes to yield an off-white solid, which was rinsed with cold 1% ethyl acetate in hexanes and then dried in vacuo to yield 1.20 g (1.68 mmol, 84.0%) of **30** as a white powder: ^1H NMR (500 MHz, C_6D_6) δ 0.84 (t, $J = 7.4$ Hz, 6H), 1.35 (m, 4H), 1.56 (m, 4H), 3.59 (t, $J = 6.5$ Hz, 4H), 6.66−6.70 (multiple resonances, 6H), 6.77 (d, $J = 8.9$ Hz, 4H), 6.92−6.94 (multiple resonances, 6H), 7.11 (d, $J = 9.0$ Hz, 4H); ^{13}C NMR (125 MHz, C_6D_6) δ 14.0, 19.5, 31.6, 67.8, 114.4, 115.8, 117.0, 118.0, 124.3, 127.7, 130.3, 132.3, 140.0, 147.3, 149.1, 156.7. Anal. Calcd for $C_{38}H_{38}Br_2N_2O_2$: C, 63.88; H, 5.36; N, 3.92. Found: C, 63.71; H, 5.20; N, 3.80.

Diaminotrimer (31). A procedure analogous to that for the preparation of **25** was employed using 1.09 g (1.52 mmol) of **26**, 0.750 g (4.55 mmol) of 4-butoxyaniline, 0.539 g (5.61 mmol) of sodium *tert*-butoxide, 82.3 mg (0.148 mmol) of bis(diphenylphosphino)ferrocene, 16.4 mg (0.073 mmol) of $Pd(OAc)_2$, and 10 mL of toluene. Chromatography of the crude product on silica with a gradient of 5−10% EtOAc in hexanes resulted in a slightly brownish resin that rapidly darkened in air. This resin was then taken into a drybox, dissolved in 1 mL of ether, and filtered through a plug of silica to remove the oxidized material. The solvent was removed in vacuo, and the residue was heated in a Kugelrohr oven overnight at 50 °C under a 5 mTorr vacuum, yielding 0.878 g (0.984 mmol, 64.7%) of **31** as a brownish resin: ^1H NMR (500 MHz, C_6D_6) δ 0.81−0.86 (multiple resonances, 12H), 1.31−1.39 (multiple resonances, 8H), 1.54−1.61 (multiple resonances, 8H), 3.58 (t, $J = 6.3$ Hz, 4H), 3.66 (t, $J = 6.5$ Hz, 4H), 4.77 (s, 2H), 6.69 (d, $J = 8.5$ Hz, 4H), 6.74 (d, $J = 9.0$ Hz, 4H), 6.78 (dd, $J_d = 8.0$ Hz, 2.0 Hz, 2H), 6.82 (d, $J = 9.1$ Hz, 4H), 6.85 (d, $J = 9.0$ Hz, 4H), 7.04 (t, $J = 8.1$ Hz, 1H), 7.12 (d, $J = 8.8$ Hz, 4H), 7.16−7.20 (multiple resonances, 5H); ^{13}C NMR (125 MHz, C_6D_6) δ 13.9 (two overlapping resonances), 19.5, 19.6, 31.6, 31.7, 67.7, 67.9, 114.3, 114.8, 115.5, 115.6, 117.7, 121.3, 126.5, 126.7, 129.9, 136.8, 140.9, 141.0, 141.4, 150.1, 154.9, 155.7. Anal. Calcd for $C_{58}H_{66}N_4O_4$: C, 78.88; H, 7.53; N, 6.34. Found: C, 78.66; H,7.44; N, 6.14.

Dibromopentamer (32). A procedure analogous to that for the preparation of **24** was employed using 0.574 g (0.643 mmol) of **31**, 0.184 g (2.00 mmol) of sodium *tert*-butoxide, 28.3 mg (0.0.0511 mmol) of bis(diphenylphosphino)ferrocene, 5.9 mg (0.018 mmol) of $Pd(OAc)_2$, and 6 mL of 1,3-dibromobenzene in a 50 mL screw-capped test tube. The crude product was chromatographed on silica with 2% EtOAc in hexanes to yield a yellowish resin, which was heated in a Kugelrohr oven overnight at 50 °C under a 5 mTorr vacuum to remove residual solvent, yielding 0.570 g (0.478 mmol, 74.3%) of **32** as a yellowish resin: ^1H NMR (500 MHz, C_6D_6) δ 0.81−0.84 (multiple resonances, 12H), 1.31−1.36 (multiple resonances, 8H), 1.52−1.58 (multiple resonances, 8H), 3.56−3.59 (multiple resonances, 8H), 6.70−6.73 (multiple resonances, 8H), 6.75 (s, 1H), 6.77 (dd, $J_d = 8.1$ Hz, $J_d = 2.0$ Hz, 4H), 6.90 (dm, $J_d = 7.5$ Hz, 2H), 6.93−6.99 (multiple resonances, 9H), 7.04 (d, $J = 8.9$ Hz, 4H), 7.09−7.12 (multiple resonances, 6H), 7.40 (t, $J = 2.0$ Hz, 2H); ^{13}C NMR (125 MHz, C_6D_6) δ 13.9, 14.0, 19.5 (two overlapping resonances), 31.6, 31.7, 67.7 (two overlapping resonances), 115.7, 115.9, 116.0, 116.8, 119.5, 123.4, 123.7, 123.8, 124.5, 125.7, 127.7, 127.8, 130.1, 130.6, 140.1, 140.6, 141.9, 144.1, 149.5, 150.6, 156.4, 156.7. Anal. Calcd for $C_{70}H_{72}Br_2N_4O_4$: C, 70.47; H, 6.08; N, 4.49. Found: C, 70.21; H, 5.93; N, 4.49.

Polymerization of 31 with 32. In a drybox, a 1 dram vial was charged with 0.1715 g (0.1940 mmol) of **31**, 0.2317 g (0.1940 mmol) of **32**, 59.9 mg (0.582 mmol) of sodium *tert*-butoxide, 194 μL of a benzene stock solution that was 0.01 mM in $Pd(OAc)_2$ and 0.03 mM in **8**, an additional 200 μL of benzene, and a stirbar. The vial was sealed with a Teflon-lined serum cap, removed from the drybox, and placed in a 90 °C oil bath for 3 days. Using the general procedure, the polymer was extracted with toluene resulting in the isolation of 266.0 mg (0.139 mmol, 71.9% yield) of polymer **33** as a white filmy solid. Removal of the majority of cyclic impurities was achieved by filtration through a 12 in. × 1.5 in. column of Sephadex LH-60 SEC resin (with THF as eluent). The resulting polymer was isolated as before (53.6% recovery) and extracted with hexanes using a Soxhlet apparatus for 3 h to remove BHT and other impurities from the product: ^1H NMR (500 MHz, $CDCl_3$) δ 0.95 (t, $J = 7.5$ Hz, 6H), 1.45 (m, 4H), 1.70 (m, 4H), 3.87 (t, $J = 6.4$ Hz, 4H), 6.46 (dd, $J_d = 8.0$ Hz, 1.5 Hz, 2H), 6.67 (s, 1H), 6.75 (d, $J = 9.0$ Hz, 4H), 6.85 (s, 4H), 6.95−6.98 (multiple resonances, 5H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 13.9, 19.2, 31.4, 67.8, 114.8, 115.1, 115.6, 124.4, 126.5, 129.3, 140.4, 142.4, 148.9, 155.3. Anal. Calcd for $C_{32}H_{34}N_2O_2$: C, 80.30; H, 7.16; N, 5.85. Found: C, 76.12; H, 6.57; N, 5.71; Ash, 1.77.

Oxidation of Polymers with Bis(trifluoroacetoxy)iodobenzene, General Procedure. In a drybox, 0.010 mmol of polymer was weighed into a 1.0 mL volumetric flask. The flask was filled with dichloromethane to provide a 0.010 M solution. This solution was diluted 1:100 and 2 mL of this solution was placed into a UV−vis cuvette. Increments of between 2.0 and 4.0 μL (0.020−0.040 μmol, 0.10−0.20 equiv) of a 0.010 M solution of bis(trifluoroacetoxy)iodobenzene in dichloromethane were added to the polymer solution in the drybox. The cuvette was removed from the drybox after each addition and the oxidation was monitored by UV−vis spectroscopy.

JA990632P