Regiodefined Poly(*N*-arylaniline)s and Donor−Acceptor Copolymers via Palladium-Mediated Amination Chemistry

Felix E. Goodson and John F. Hartwig*

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

Received January 7, 1998

Oligomeric and polymeric arylamines display important conductive and magnetic properties. In 1985, it was shown that doped polyaniline, which is readily synthesized by chemical[1] or electrochemical[2] oxidation of aniline, is capable of conducting electricity in the metallic regime.[3] The air and water stability of this material in the conductive form[3] permits applications as electrodes in lightweight batteries[4,5] and flexible, hole-injecting electrodes in electroluminescent devices.[6] However, it is unlikely that poly(*p*-aniline) and substituted polyanilines[7−9] contain exclusively para C−N linkages between monomers. Furthermore, the radical couplings that produce poly(*p*-aniline) cannot produce *m*-substituted versions and cannot produce alternating copolymers. Recently, poly(*m*-aniline)[10−13] and oligoaniline derivatives with alternating *meta* and *para* regiochemistry[14] have received attention as possible candidates for organic ferromagnetic applications. Poly(*m*-aniline) and its derivatives have been synthesized by the copper-mediated Ullmann coupling,[10,13] but insoluble fractions (which may be due to cross-linking)[11] and regioirregularities[15] result from this synthetic methodology. Donor−acceptor polymers have received increased attention recently due to their low band gaps, luminescence, and potential third-order nonlinear optical properties.[16]

A general methodology to prepare polyaniline derivatives with well-defined regiochemistry and copolymers with electronically cooperative monomers would be an important synthetic advance in arylamine polymer synthesis. Recent research by Buchwald's group[17] and our group[18,19] has generated highly efficient methods to prepare aromatic amines from primary or secondary amines and aryl bromides. This reaction has been used to generate poly(arylenamines) with saturated alkyl spacers in the polymer backbone[20] and, during the course of the work reported here, parent poly(*m*-aniline).[21] We report the palladium-catalyzed preparation of unsaturated polymeric triarylamines and triarylamine copolymers that are regiodefined and that cannot be prepared by oxidative methods. Arylamine polymers with high molecular weights were prepared after evaluation of concentration effects and their impact on the relative rates for polymer growth vs cyclization.

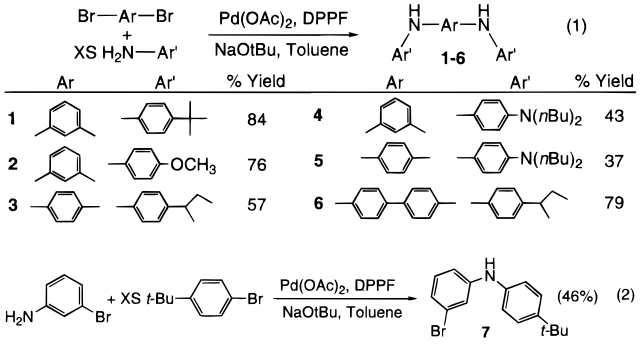
Bis(amine) monomers **1**−**6** were conveniently synthesized by using a combination of $Pd(OAc)_2$ and DPPF (eq 1).[22] Reaction of the appropriate dihalide with an excess of aromatic amine led to the desired monomers, which were readily purified by chromatography and recrystallization. The 3-bromoaniline monomer **7** was similarly synthesized from 3-bromoaniline and a large excess of 4-*tert*-butylbromobenzene (eq 2).

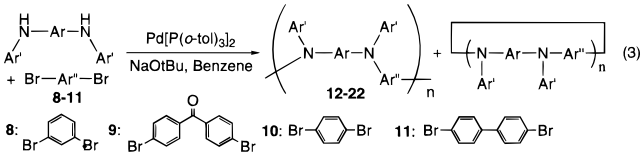
Polymerizations (eq 3) between **1**−**6** and commercially available aromatic dibromides **8**−**11**, as well as self-condensations of the 3-bromoaniline monomer **7**, were performed under a variety of conditions to form polymers **12**−**22**. The resulting data on molecular weights and yields are provided in Table 1. Initial reactions involving the combination of monomers **1** and **8** (entry 1) resulted in the formation of oligomeric materials, as evidenced by low molecular weight, multimodal GPC traces and complicated ^1H and ^{13}C NMR spectra. We have shown previously that reactions of electron-poor aryl halides and electron-rich amines give the highest yields in the amination chemistry.[23] Thus, we attempted polymerizations of monomers **1** and **2** at 0.02 M with the electron-poor dibromobenzophenone **9**. Again,

Table 1. Molecular Weight Data and Yields for Polymerizations of Different Monomers at Varying Concentrations[a]

run	monomers	polymer	conc[b]	yield (%)	M_n[c]	M_w[c]	DP[d]
1	**1**, **8**	**12**	0.024	39	1798	3065	8
2	**1**, **8**	**12**	1.0	55	3353	7231	15
3	**1**, **8**	**12**	2.0	53	4016	10212	18
4	**1**, **9**	**13**	0.02	90	2801	6538	10
5	**1**, **9**	**13**	0.05	65	3533	10747	13
6	**1**, **9**	**13**	1.0	95	9016	42178	32
7	**1**, **9**	**13**	2.5	45	3289	10472	14
8	**1**, **10**	**14**	1.0	52	2908	5836	13
9	**1**, **10**	**14**	2.0	39	3134	7700	14
10	**2**, **9**	**15**	0.02	67	2149	6050	9
11	**2**, **9**	**15**	0.10	85	4078	17400	16
12	**3**, **8**	**16**	2.0	65	2451	10907	11
13	**3**, **9**	**17**	0.10	83	5736[e]	29741[e]	20
14	**3**, **10**	**18**	2.0	81	6172	17682	28
15	**4**, **9**	**19**	1.0	82	10442	29631	30
16	**5**, **9**	**20**	1.0	82	13617	45406	39
17	**6**, **9**	**21**	1.0	93	11603	35753	37
18	**6, 11**	**22**	1.0	57	6955	24366	23
19	**7**	**12**	2.0	83	2703	5761	12

[a] Polymerizations run at 90 °C for 3d in the presence of 2% bis[tris(*o*-tolyl)phosphine]palladium(0), 2% tris(*o*-tolyl)phosphine, and 1.5 equiv sodium *tert*-butoxide. [b] Concentration in millimoles of monomer per milliliter of solvent added. [c] As determined by gel permeation chromatography in THF relative to polystyrene standards. As GPC is a relative technique, it should be mentioned that these numbers are relative and do not reflect true values. [d] Number-averaged degree of polymerization indicating the average number of couplings per polymer chain (i.e., DP = 2*n* (eq 3)). [e] GPC analysis performed in chloroform.





S0024-9297(98)00027-8 CCC: $15.00
Published on Web 02/19/1998

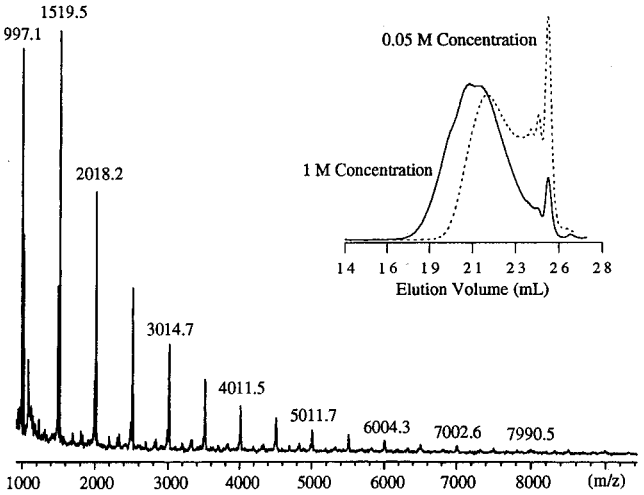


Figure 1. MALDI-TOF spectrum for polymer **15** (Table 1, entry 11), revealing the presence of cyclic oligomers. Inset: GPC chromatograms for polymer **13** synthesized under dilute (Table 1, entry 5) and concentrated (Table 1, entry 6) conditions.

we obtained oligomeric material (entries 4 and 10), suggesting that the yields of C−N bond formation were not the dominant factor in limiting polymer molecular weight.

Reaction between monomers **1** and **9** at a concentration of 1 M produced polymeric material (entry 6). This concentration provided the highest molecular weights for this polymerization; reaction of **1** and **9** (entry 7) at 2 M concentration gave lower molecular weights. Monomer **2** was not soluble enough for reaction at these concentrations, but molecular weights from reaction of **2** and **9** at 0.2 M gave higher molecular weights than reaction at 0.1 M (entry 11). The ^{1}H and ^{13}C NMR spectra of the polymers from these reactions were well-resolved. Figure 1 (inset) shows GPC traces for polymer **13** formed under dilute and concentrated conditions. Clearly, the amount of low molecular weight material decreases as the concentration of the reaction solution increases. The yields and molecular weights listed in Table 1 were determined after precipitative workup. However, GPC traces before and after workup were similar (M_n ca. 12% lower before precipitation for entry 6), suggesting that the workup did not eliminate oligomeric material.

This effect of reaction concentration on product molecular weight led us to consider that polymerization was terminated by formation of cyclic oligomers and that the sharp GPC peaks at low molecular weight were due to macrocycles. The synthesis of analogous cyclic oligomers of other aromatic polymers have been reported,[24−28] and cyclic oligomers of PEEK (a poly(aryl ether ketone)) have been isolated from a commercial sample.[29] Indeed, when **2** was reacted with **9** under extremely dilute conditions (0.001 M), a macrocycle, **23**, with two units of each component monomer ($n = 2$ for the cyclic product in eq 3) was isolated in 17% yield after purification by chromatography and recrystallization. X-ray diffraction and mass spectrometry clearly identified the cyclic structure and the number of monomer units in **23**.

MALDI-TOF spectrometry (Figure 1) of polymer **15** (entry 11) provided further evidence for substantial formation of cyclic products under dilute conditions. Signals were observed at *m/z* 997, 1519, 2018, etc. that corresponded to the proton adduct of **23** and the sodium adducts of the cyclic hexamer, octamer, etc., respectively. The absence of accompanying signals for odd-numbered oligomers such as amine-centered trimer (*m/z* = 681), amine-centered pentamer (*m/z* = 1276), amine-centered heptamer (*m/z* = 1636), bromide-centered trimer (*m/z* = 819), bromide-centered pentamer (*m/z* = 1179), or bromide-centered heptamer (*m/z* = 1756)[30] (or signals due to proton and/or sodium adducts) argues strongly for the cyclic nature of these materials. The absence of signals due to both low and high molecular weight linear chains may be due to chain entanglement, which would be less severe for the macrocycles. Alternatively, phosphine end caps (vide infra) may hinder ionization of the linear chains.

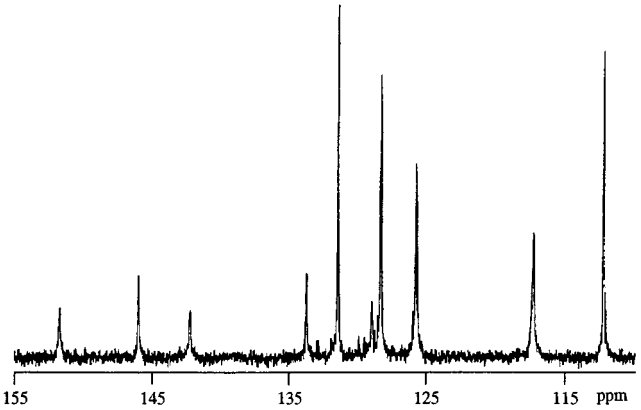


Figure 2. Aromatic region of the ^{13}C NMR spectrum for polymer **20**.

Monomer geometry influenced the amount of cyclization that occurred. *p*-Diaminobenzene monomers **3** and **5** and *p*-dibromobenzene monomer **10** appeared to be less susceptible to the cyclization than their *meta* analogues (compare entries 3 and 14). Biphenyl monomers **6** and **11** also gave polymeric material. However, all of the polymers showed some contamination of the linear material with cyclic oligomers, as evidenced by the multimodal GPC chromatograms. The aromatic region of the ^{13}C NMR spectrum for polymer **20** is presented in Figure 2, showing the expected 10 resonances and providing evidence for the structural regularity of the polymer.

Electronic properties of the monomers did have an effect on molecular weight when the polymerizations were run at optimal concentrations. Use of the electron-rich bis(amine) monomers **4** and **5** resulted in a slight improvement in molecular weight (entries 15−17), and polymer **20** was obtained with a DP near 40, an M_n of 13 600, and an M_w of 45 406 (entry 16). Polymerizations with dibromobenzene monomers **8** and **10** (entries 1−3, 8−9, 12, and 14) could be carried out at concentrations as high as 2 M before the molecular weight dropped. However, the molecular weights were significantly lower than those for polymers synthesized from electron-poor monomer **9**.

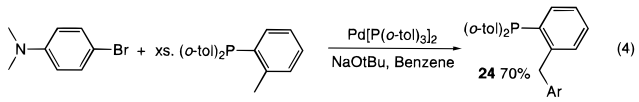
^{31}P NMR spectrometry of **13** showed that some phosphine is incorporated into the material. Exchange of palladium-bound and phosphine aryl groups in arylpalladium(II) bis(phosphine) complexes[31] has caused phosphine incorporation in palladium-mediated poly(*p*-phenylene) polymerizations.[32] However, tris(*o*-tolyl)phosphine has been shown to resist aryl exchanges;[33] therefore, phosphine incorporation is unlikely to occur by P−C bond cleavages. Instead, arylation of the *o*-tolyl

Table 2. UV/Vis, Fluorescence, and Thermal Characterization of Polymers

polymer	λ_{max}[a]	Ex_{max}[b]	Em_{max}[c]	T_{D1}[d]	T_{D2}[d]	char yield[e] (%)
13	390	452	506	350	530	62
18	339	*f*	*f*	348	566	59
19	402	*f*	*f*	210	472	58
20	416	*f*	*f*	245	422	58
21	400	471	523	120	559	66
22	376	422	437	300	609	65

[a] Wavelength of maximum absorbance (UV/vis). [b] Wavelength of maximum fluorescence excitation. [c] Wavelength of maximum fluorescence emission. [d] See text. [e] Percent mass remaining at 800 °C (TGA, N_2). [f] No fluorescence was observed.

positions[34] is the more likely route to phosphine incorporation in our material. Reaction of *N*,*N*-dimethyl-4-bromoaniline with an excess of tris(*o*-tolyl)phosphine under the basic conditions of the amination reaction, led to the arylated phosphine **24** in 70% yield (eq 4).



(4)

Because the molecular weight data of the polymers is not anomalously high relative to predicted molecular weights from known reaction yields, cross-linking through the phosphorus atoms by *o*-tolyl arylation is probably not a significant occurrence in these polymerizations. Although a small amount of branching through phosphine moieties may contribute to the large polydispersities, the presence of low molecular weight cyclic material probably has a larger effect on these values. Thus, chain termination is likely to be the most significant consequence of this phosphine arylation.

With the exception of polymers **17** and **22**, which are only slightly soluble in THF and moderately soluble in $CHCl_3$, the polymers exhibit good solubility in common organic solvents such as THF, $CHCl_3$, and benzene. The donor−acceptor polymers are all bright yellow or orange, and polymers **13**, **15**, **21**, and **22** exhibit strong fluorescence, making them possible candidates for emissive components in electroluminescent devices. UV−vis and fluorescence spectroscopy data are presented in Table 2, along with data obtained from thermal gravimetric analysis (TGA). In general, TGA analysis showed a two-step decomposition, the first resulting in a 5−10% weight loss (onset labeled T_{D1}) and the second resulting in carbonization of the material (T_{D2}).

In conclusion, we have used palladium-mediated amination chemistry to synthesize arylamine polymers with M_n values as high as 13 600 and M_w values of 45 000. Molecular weights are predominantly limited by formation of macrocycles, and this cyclization has been reduced by conducting the polymerizations at high concentrations (ca. 1 M). Studies on small molecules suggest that reduction of the aryl halide to form arene does compete with cyclization as a molecular weight limiting process for polymerizations that produce electron-rich aryl halide intermediates.[35] Efforts toward minimizing the competing reduction and phosphine incorporation, as well as studies on further optimizing these polymerizations, are currently underway.

Acknowledgment. We are grateful to the Department of Energy for support of this work. Initial studies were made possible through support from an NSF Young Investigator Award, a DuPont Young Professor Award, a Union Carbide Innovative Recognition Award, and a Camille Dreyfus Teacher-Scholar Award. J.F.H. is a Sloan Foundation Fellow. We thank Johnson Matthey Alfa/Aesar for a loan of palladium acetate and Prof. Bruce M. Novak for the use of GPC equipment.

Supporting Information Available: Experimental methods for monomer synthesis and polymerization reactions. Spectroscopic and analytical data of monomers, polymers **12**−**22**, and cyclic oligomer **23** and arylated phosphine **24**(10 pages). Ordering and Internet access information is given on any current masthead page.

References and Notes

(1) 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.
(2) Diaz, A. F.; Logan, J. A. *J. Electroanal. Chem.* **1980**, *11*, 111.
(3) 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.
(4) MacDiarmid, A. G.; Mu, S. L.; Somasiri, M. L. D.; Wu, W. *Mol. Cryst. Liq. Cryst.* **1985**, *121*, 187.
(5) Kitani, A.; Kaya, M.; Sasaki, K. *J. Electrochem. Soc.* **1986**, *133*, 1069.
(6) Gustafsson, G.; Cao, Y.; Treacy, G. M.; Klavetter, F.; Colaneri, N.; Heeger, A. J. *Nature* **1992**, *357*, 477.
(7) Mattoso, L. H. C.; Faria, R. M.; Bulhões, L. O. S.; MacDiarmid, A. G. *J. Polym. Sci., Polym. Chem. Ed.* **1994**, *32*, 2147.
(8) Wei, Y.; Hariharan, R.; Patel, S. A. *Macromolecules* **1990**, *23*, 758.
(9) Leclerc, M.; Guay, J.; Dao, L. H. *Macromolecules* **1989**, *22*, 649.
(10) Ito, A.; Ota, K.; Tanaka, K.; Yamabe, T.; Yoshizawa, K. *Macromolecules* **1995**, *28*, 5618.
(11) Yoshizawa, K.; Ito, A.; Tanaka, K.; Yamabe, T. *Solid State Commun.* **1993**, *87*, 935.
(12) Yoshizawa, K.; Tanaka, K.; Yamabe, T. *Chem. Lett.* **1990**, 1311.
(13) Ishida, T.; Iwamura, H. *Chem. Lett.* **1991**, 317.
(14) Wienk, M. M.; Janssen, R. A. J. *J. Am. Chem. Soc.* **1997**, *119*, 4492.
(15) Yoshizawa, K.; Ito, A.; Tanaka, K.; Yamabe, T. *Synth. Met.* **1992**, *48*, 271.
(16) Zhang, Q. T.; Tour, J., M. *J. Am. Chem. Soc.* **1997**, *119*, 5065 and references therein.
(17) Guram, A. S.; Rennels, R. A.; Buchwald, S. L. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1348.
(18) Louie, J.; Hartwig, J. F. *Tetrahedron Lett.* **1995**, *36*, 3609.
(19) Hartwig, J. F. *Synlett* **1997**, 329.
(20) Kanbara, T.; Honma, A.; Hasegawa, K. *Chem. Lett.* **1996**, 1135.
(21) Kanbara, T.; Izumi, K.; Nakadani, Y.; Narise, T.; Hasegawa, K. *Chem. Lett.* **1997**, 1185.
(22) Driver, M. S.; Hartwig, J. F. *J. Am. Chem. Soc.* **1996**, *118*, 7217.
(23) Hartwig, J. F.; Richards, S.; Barañano, D.; Paul, F. *J. Am. Chem. Soc.* **1996**, *118*, 3626.
(24) Colquhoun, H. M.; Dudman, C. C.; Thomas, M.; O'Mahoney, C. A.; Williams, D. J. *J. Chem. Soc., Chem. Commun.* **1990**, 336.
(25) Brunelle, D. J.; Shannon, T. G. *Macromolecules* **1991**, *24*, 3035.
(26) Ganguly, S.; Gibson, H. W. *Macromolecules* **1993**, *26*, 2408.
(27) Wang, Y.-F.; Chan, K. P.; Hay, A. S. *Macromolecules* **1995**, *28*, 6371.
(28) Jiang, H.; Chen, T.; Xu, J. *Macromolecules* **1997**, *30*, 2839.
(29) Jonas, A.; Legras, R. *Macromolecules* **1993**, *26*, 2674.
(30) These mass assignments were made under the assumption that what aryl halide was not consumed by the polymerization reaction was consumed by the competing reduction to form arene (vide infra). This assumption was borne out by the fact that there was less than 0.05% bromine by elemental analysis for **13**.
(31) Kong, K.-C.; Cheng, C.-H. *J. Am. Chem. Soc.* **1991**, *113*, 6313.

(32) Wallow, T. I.; Seery, T. A. P.; Goodson, F. E.; Novak, B. M. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1994**, *35*, 710.
(33) Herrmann, W. A.; Brossmer, C.; Öfele, K.; Beller, M.; Fischer, H. *J. Mol. Catal. A.: Chem.* **1995**, *103*, 133.
(34) Louie, J.; Hartwig, J. F. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 2359.
(35) Goodson, F. E.; Hartwig, J. F. Unpublished results.

MA980027R