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Preparation of non-Kekulé- and nondisjoint-type aromatic polyamines by palladium-catalyzed polycondensation and their poly(cationic radical)s

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Abstract

A series of triarylamine polymers were prepared by palladium-catalyzed polycondensation. Extension of the π-conjugation was analyzed by UV and electrochemical measurements, which revealed the degree of off-coplanarity in the polymer framework. Chemical oxidation of the polymer with $NOPF_6$ gave the corresponding poly(aminium cationic radical). The ESR signal at room temperature indicated an exchange interaction between the radicals in the polymer. The spectrum recorded at 12 K displayed a $\Delta M_s = \pm 2$ transition signal at half-field, which was characteristic of multiplet species.

Keywords: Aromatic polyamine; Polycondensation; Aminium cationic radical; Non-Kekulé molecule; Palladium-catalyzed amination

1. Introduction

The concern with studies of high-spin molecules and organic ferromagnets has been growing over the past several decades [1,2]. In particular, the aromatic polyamine group has been an attractive material for tractable high-spin polyradicals, because the triarylaminium cationic radical has both a substantial stability at room temperature (r.t.) and robust spin polarization effect. Since Torrance et al. reported the specific preparation of poly(1,3,5-triaminobenzene) and its ferromagnetic behavior up to 400 °C in 1987 [3], much effort to synthesize diarylamine and triarylamine polymers with a well-defined non-Kekulé and nondisjoint structure has been made. Tanaka et al. synthesized poly(*m*-aniline) and its derivatives using the copper Ullmann reaction [4]. However, Ullmann chemistry generally requires drastic conditions such as high temperature and a long reaction time to give the desired product in modest yield. The recent development of palladium-catalyzed amination chemistry made it possible to synthesize complicated aromatic polyamines under mild conditions in high yield [5,6]. Hartwig et al. reported the synthesis of high molecular weight triarylamine polymers and dendrimers using a multistep growth strategy and the triplet character of the corresponding poly(cationic radical)s [7,8]. Linear and hyperbranched poly(*m*-aniline)s with little structural defects were also synthesized via one-pot polycondensations by other groups [9,10].

During the course of polyradical investigations, the two-dimensional extension of π-conjugation in a non-Kekulé and nondisjoint fashion has brought about an increase in the spin quantum number (S). For example, Rajca et al. achieved an exceedingly high S value of $>$ 5000 for the calix[4]arene-based network polyradical prepared by the condensation of two tetrafunctionalized subparts [11]. Bushby et al. synthesized triarylamine network polymers using the Suzuki coupling reaction [12,13]. The corresponding poly(aminium cationic radical) displayed an S value of 4 in spite of the cross-conjugated structure. We reported a relatively high S value of 5 for the poly(4-phenoxyl-1,2-phenylenevinylene) planarily extended by the Heck polycondensation [14]. The polycondensation of two multi-functionalized

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Table 1
Polycondensation result of 1,3,5-tris(anisylamino)benzene **1** and 1,3,5-tribromobenzene **2** using various catalysts [a]

Run	[**1**](M)	[**2**](M)	Catalyst	Ligand	Time (h)	M_w [b]	M_w/M_n [b]
1	0.72	0.72	$Pd_2(dba)_3$	BINAP	72	1200	1.1
2	0.72	0.72	$Pd_2(dba)_3$	P(*o*-tolyl)$_3$	6	gel	
3	0.72	0.72	$Pd_2(dba)_3$	P(*t*-Bu)$_3$	0.17	gel	
4	0.72	0.72	$Pd(OAc)_2$	P(*t*-Bu)$_3$	1	gel	
5	0.015	0.030	$Pd_2(dba)_3$	P(*t*-Bu)$_3$	0.33	gel, 8300 [c]	1.6 [c]

[a] Polymerizations were carried out in the presence of 4.5 equiv. NaO*t*Bu for **1**, 4 mol% Pd for **1**, and phosphine ligand ([Pd]/[P] = 1/3) in toluene at 100 °C.

[b] Number- and weight-average molecular weight measured by GPC.

[c] Trace amounts of soluble fraction in CH_2Cl_2.

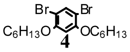
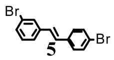
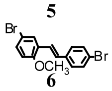
monomers is advantageous over the self-condensation of a monomer bearing two kinds of functional groups, because the molecular weight or the degree of polymerization and the terminal groups of the resulting polymer can be easily controlled by the feed ratio of the two monomers. In this paper, we noted that the cationic triradical of 1,3,5-tris(dianisylamino)benzene **3** has been investigated in detail to be a quartet ground state molecule [15,16], that is, we selected 1,3,5-tris(anisylamino)benzene **1** as a three-functionalized triradical subpart and extended it to a series of pseudo-two-dimensional triarylamine network polymers by the palladium-catalyzed polycondensation with an aryl di- or tri-halide. The electrochemical and magnetic properties of the corresponding poly(cationic radical)s were also discussed.

2. Results and discussion

1,3,5-Tris(anisylamino)benzene **1** and 1,3,5-tribromobenzene **2** were polymerized using a palladium–phosphine catalyst in toluene at 100 °C (Table 1). The polymerization for the feed ratio of [*sec*-amine]/[bromide] = 1 with $Pd_2(dba)_3$ as the catalyst and BINAP as the bulky ligand gave only an oligomer even after 3 days. However, the use of P(*o*-tolyl)$_3$ and P(*t*-Bu)$_3$ under the same conditions afforded a yellow gel in 6 h and 10 min, respectively. Judging from the superiority of $Pd_2(dba)_3$ to $Pd(OAc)_2$, the combination of $Pd_2(dba)_3$ and P(*t*-Bu)$_3$ was proven to be the most active catalyst system in the present study. Dilution of the total monomer concentration and the feed ratio of [*sec*-amine]/[bromide] = 1/2 not to include any diarylamine structures in the polymer enabled us to obtain a solvent-soluble triarylamine polymer with the average molecular weight of 8300. The absence of an amine proton in the IR and ^1H NMR spectra of the polymer and resemblance of the CP-MAS ^{13}C NMR spectrum of the insoluble portion to that of **3** suggested that the produced polymer certainly consisted of the two-dimensional network structure of **3** (Scheme 1).

Aryl dibromides, which are expected to act as a ferromagnetic coupler in the polymer framework, were also subjected to the polycondensation reaction with **1**. *m*-Phenylene and *m,p′*-stilbenoid skeletons have been shown to ferromagnetically connect two diarylaminium cationic radicals [17,18]. The aryl dibromides and **1** were reacted in the feed ratio of [*sec*-amine]/[bromide] = 1/2 using the combination of $Pd_2(dba)_3$ and P(*t*-Bu)$_3$ in toluene at 100 °C for 24 h (Table 2). According to Flory's theorem, the polycondensation of a trifunctionalized monomer (3A) and bifunctionalized monomer (2B) with the feed ratio [A]/[B] = 1/2 provides a polymer with an infinite molecular weight and terminal B groups [19]. The reaction of **1** and **4** at 0.2 and 0.6 M, respectively, gave poly-**2** with a molecular weight of 5000. A longer reaction time did not improve the molecular weight and yield. On the other hand, the reaction of **1** with **5** or **6** at the same concentration gave poly-**3** or poly-**4** with the higher molecular weight of 12 700 and 10 900, respectively. The IR and ^1H NMR measurements indicated the disappearance of the secondary amines in **1** and all the terminal bromide groups for poly-**3** and poly-**4**. These results reveal that the reaction of an aryl halide bearing an electron donating

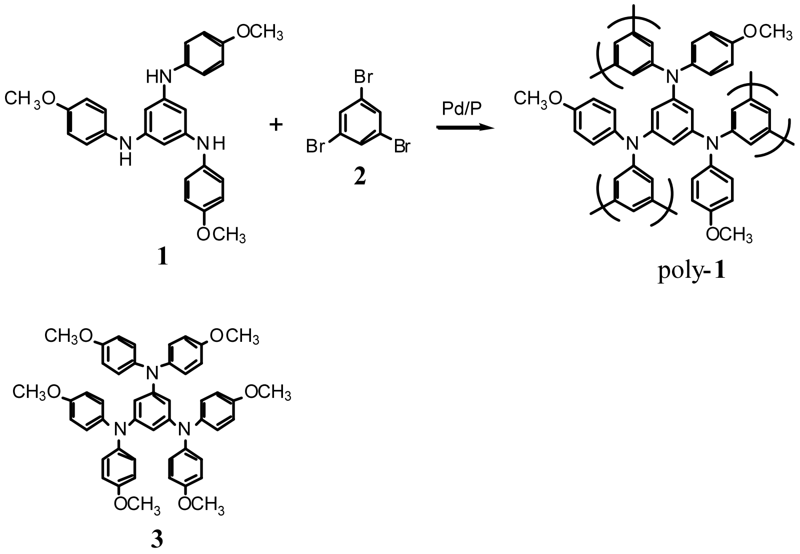
Table 2
Polycondensation result of 1,3,5-tris(anisylamino)benzene **1** and aryl dihalide [a]

Run	Aryl dihalide	Polymer	[**1**] (M)	Yield (%)	M_w [b]	M_w/M_n [b]
1	 **4**	poly-**2**	0.20	11	5000	1.4
2	**4**	poly-**2**	0.0067	c	gel	-
3	 **5**	poly-**3**	0.20	69	12700	2.8
4	**5**	poly-**3**	0.0067	c	gel	-
5	 **6**	poly-**4**	0.20	65	10900	2.2

[a] Polymerizations were carried out in the presence of 4.5 equiv. NaO*t*Bu for **1**, 2 mol% $Pd_2(dba)_3$ for **1**, and 12 mol% P(*t*-Bu)$_3$ with the feed ratio of [**1**]/[**4** (**5**, **6**)] = 1/3 in toluene at 100 °C for 24 h.

[b] Number- and weight-average molecular weight measured by GPC.

[c] Most of polymerization products were methanol soluble oligomer. The quantity of gel was too small to be weighed.



Scheme 1.

substituent and aryl amine is difficult to complete in high yield. Both reactions at the lower concentration of 0.0067 M for **1** produced insoluble polymers or a gel. This concentration dependence suggested the occurrence of cyclic oligomers with a low solubility during the polycondensation.

The UV spectra of poly-**1** and poly-**2** exhibited strong absorption peaks attributable to the triarylamine moiety at 298 and 295 nm, respectively, while those of poly-**3** and poly-**4** showed two peaks at 305 and 380 nm and at 301 and 386 nm, respectively (Table 3). The latter peaks for the poly-**3** and poly-**4** are ascribed to the stilbene units. All peaks based on triarylamine moiety in the polymers shift to a lower wavelength than that of the model compound **3**, which reflects the degree of off-coplanarity in the polymer framework. This result was supported by differential pulse voltammetry (DPV) measurements. The overall redox potential of the polymers was much higher than that of **3**. In addition, the peak gap between the first and the second redox potentials for **3** was 0.23 V (Fig. 1(a)), while the smaller gap for the polymers, e.g., 0.19 V for poly-**1**, was observed (Fig. 1(b)). The distorted π-conjugation and the small electronic interaction between the aminium cationic radicals resulted in the slight splitting of the redox waves for the polymer. Nevertheless, the DPV of poly-**1** displayed unequivocal waves step by step in contrast to the unresolved wave of poly-**2**, which implies that poly-**1** is composed of tightly cross-linked networks of a π-conjugated polymer with topological 1,3,5-connectivity. The first set of redox potentials for poly-**3** and poly-**4**, though broadening, exhibited results comparable to the corresponding stilbenoid diamine compounds.

Table 3
UV absorption maxima (λ_{max}) and redox potentials of **3** and the polymers

Compound	λ_{max} [a] (nm)	Redox potential [b] (V)
3	305	0.54, 0.78, 1.02, 1.12
poly-**1**	298	0.64, 0.82, 1.05, 1.24, 1.41
poly-**2**	295	0.70 [c], 1.28
poly-**3**	305, 380	0.66, 1.22
poly-**4**	301, 386	0.67, 0.82, 1.23, 1.36

[a] UV spectra were measured in CH_2Cl_2.
[b] vs. Ag/AgCl.
[c] Unresolved peak.

The chemical oxidation of the polymers using $NOPF_6$ solubilized in CH_2Cl_2 with 18-crown-6 was carried out under nitrogen at r.t. The addition of one equivalent of the oxidant to the poly-**1** solution in the presence of an adequate amount of trifluoroacetic acid and trifluoroa-

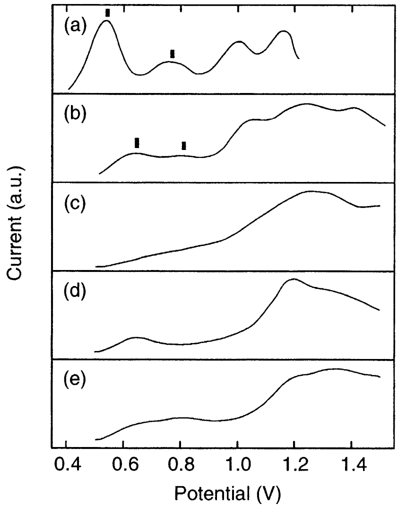


Fig. 1. DPV of **3** and the polymers (1 mM per amine unit) in CH_2Cl_2 containing 0.1 M $(C_4H_9)_4NBF_4$ at r.t. (a) **3** (b) poly-**1** (c) poly-**2** (d) poly-**3** (e) poly-**4**.

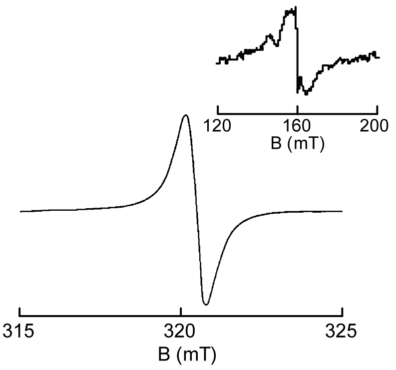


Fig. 2. ESR spectrum of poly-**1** (10 mM) oxidized with $NOPF_6$ in $CH_2Cl_2/CF_3COOH/(CF_3CO)_2O$ at r.t. Inset: $\Delta M_s = \pm 2$ transition at 12 K.

cetic anhydride gave a dark brown solution. The ESR spectrum of this solution (10 mM per amine unit) consisted of a broad single line with a peak-to-peak width of 6.3 G at $g = 2.0028$, which was ascribed to the aminium cationic radical (Fig. 2). The spectrum still showed a single line without hyperfine splitting even at 0.1 mM per amine unit due to electron exchange between the aminium cationic radicals in the polymer. The same phenomena were observed for the oxidation products of the other polymers. The ESR of poly-**1** oxidized with $NOPF_6$ in $CH_2Cl_2/CF_3COOH/(CF_3CO)_2O$ was recorded at 12 K. A $\Delta M_s = \pm 2$ forbidden transition clearly emerged at half-field with an asymmetric fine structure, which means the occurrence of multiplet states equal to or higher than a triplet for the polyradical (Fig. 2 inset). A temperature dependence experiment of the ESR signal is under way to determine the ground state of the polyradical. In any event, it has become apparent from the studies described above that the palladium-catalyzed amination chemistry can be effectively used to extend a triarylaminium cationic radical to the two-dimensional forms for a high-spin polyradical.

3. Experimental

3.1. Materials

1,3,5-Tris(anisylamino)benzene **1** and 1,3,5-tris(dianisylamino)benzene **3** were prepared according to the literature [20]. The stilbene derivatives **5** and **6** were previously described [17,18]. The other reagents were used as received. The solvents were purified in the usual manners.

3.2. 1.5-Dibromo-2,4-dihexyloxybenzene 4

2,4-Dibromoresorcinol (3.99 g, 14.9 mmol), prepared using a literature method [21], 1-bromohexane (25.9 g, 0.157 mol), and potassium carbonate (31.4 g, 0.227 mol) were added to 300 ml of ethanol solution. The solution was then refluxed with stirring for 20 h. After cooling to r.t., the deposited insoluble material was filtered off and the filtrate was evaporated. To this crude product was added 300 ml of CH_2Cl_2 and washed with aqueous sodium hydroxide and water. After drying over anhydrous sodium sulfate, the solution was evaporated and the residual product was purified by column chromatography on silica gel (hexane/chloroform = 3/1) and recycling preparative HPLC LC-918R/U (Japan Analytical Industry Co.) to give **4** as white needle crystals. Yield 72%: m.p. 52.5 °C; IR (KBr pellet) 1202, 1059 (ν_{C-O-C}); ^1H NMR ($CDCl_3$, 500 MHz) $\delta = 0.91$ (t, 6H, $J = 7$ Hz, $-CH_3$), 1.33–1.37 (m, 8H, $-CH_2-$), 1.50 (q, 4H, $J = 7$ Hz, $-CH_2-$), 1.83 (q, 4H, $J = 7$ Hz, $-CH_2-$), 3.99 (t, 4H, $J = 7$ Hz, $-OCH_2-$), 6.46 (s, 1H, ArH), 7.64 (s, 1H, ArH); ^{13}C NMR ($CDCl_3$, 125 MHz) $\delta = 13.97$, 22.54, 25.61, 29.01, 31.47, 69.72, 99.99, 103.07, 135.76, 155.67; MS m/z 434 $[(M-2)^+]$, 436 $[M^+]$, 438 $[(M+2)^+]$.

3.3. Polymerization procedure

In a 10 ml ampule tube, 1,3,5-tris(anisylaminobenzene) **1**, the aryl di- or tri-halide, sodium *tert*-butoxide (4.5 equiv. to **1**), Pd catalyst (4 mol% Pd for **1**), and phosphine ligand (12 mol% P for **1**) were added, and toluene was then added to it in the desired concentration. The tube was attached to a vacuum line, sealed off, and then heated to 100 °C in an oil bath. After cooling to r.t., the resulting crude product was treated with 5 ml of aqueous ammonia and extracted with 50 ml of CH_2Cl_2. In the course of this workup, an insoluble fraction was filtered off and washed with methanol and water. The residual organic layer was concentrated and precipitated into 50 ml of methanol to give a yellow polymer. Reprecipitation from CH_2Cl_2 into methanol was repeated until the monomer was removed.

1 (46.1 mg, 0.104 mmol) and **2** (65.5 mg, 0.208 mmol) in 7 ml of toluene were reacted for 20 min in the presence of NaO*t*Bu (45.0 mg, 0.468 mmol), $Pd_2(dba)_3$ (1.9 mg, 2.1×10^{-6} mol), and $P(t\text{-}Bu)_3$ (2.5 mg, 1.2×10^{-5} mol) to give 24.2 mg of poly-**1** (Table 1, run 5). ^1H NMR of the CH_2Cl_2 soluble fraction (THF-d_4, 500 MHz) $\delta = 3.6$–3.7 (brs, $-OCH_3$), 5.8 (s, 1,3,5-benzenetriyl), 6.5–7.1 (m, ArH); CP-MAS ^{13}C NMR (100 MHz) $\delta = 55.1$, 105.6, 111.8, 114.8, 126.5, 128.9, 136.0, 138.1, 140.3, 149.3, 156.3.

1 (0.265 g, 0.600 mmol) and **4** (0.785 g, 1.80 mmol) in 3 ml of toluene were reacted for 24 h in the presence of NaO*t*Bu (0.259 g, 2.70 mmol), $Pd_2(dba)_3$ (11.0 mg, 1.20×10^{-5} mol), and $P(t\text{-}Bu)_3$ (14.5 mg, 7.2×10^{-5} mol). After two reprecipitations, 0.100 g of poly-**2** was obtained. Yield 11%: ^1H NMR (C_6D_6, 600 MHz) $\delta =$

0.8–1.7 (m, $-CH_2-$ and $-CH_3$), 3.2–3.8 (m, $-OCH_2-$ and $-OCH_3$), 6.0–7.8 (m, ArH).

1 (0.265 g, 0.600 mmol) and **5** (0.608 g, 1.80 mmol) were reacted in a similar manner to give 0.503 g of poly-**3**. Yield 69%: ^{1}H NMR (C_6D_6, 600 MHz) $\delta = 3.2–3.3$ (m, $-OCH_3$), 6.2–7.7 (m, ArH and CH=CH).

1 (0.265 g, 0.600 mmol) and **6** (0.663 g, 1.80 mmol) were reacted in a similar manner to give 0.782 g of poly-**4**. Yield 65%: ^{1}H NMR (C_6D_6, 500 MHz) $\delta = 3.2_0$ (s, $-OCH_3$), 3.2_2 (s, $-OCH_3$), 6.2–7.5 (m, ArH and CH=CH).

3.4. Oxidation

A CH_2Cl_2 solution (0.44 ml) of $NOPF_6$ (10 μmol; 1.0 equiv. to the amine unit) solubilized with a minimum amount of 18-crown-6 was added to a CH_2Cl_2/CF_3COOH/$(CF_3CO)_2O$ (90/9.5/0.5 v/v/v) solution (0.56 ml) of the polymer (10 μmol per amine unit) under nitrogen in a glove box. The solution rapidly turned dark brown, but it was stirred for further 5 min to complete the reaction and used for the ESR measurements.

3.5. Measurements

DPV was carried out with a BAS 100B/W electrochemical analyzer in CH_2Cl_2 solution of 0.1 M $(C_4H_9)_4NBF_4$ as a supporting electrolyte. A platinum working electrode and a commercial Ag/AgCl electrode as the reference were used. The formal potential of the ferrocene/ferrocenium couple was 0.43 V vs. this reference electrode. The sample solution was under an argon atmosphere during the measurement: The pulse width was 50 mV.

ESR spectra were taken using a JEOL JES-2XG ESR spectrometer with 100-kHz field modulation. The IR, NMR, mass, and UV spectra were measured with JASCO FT/IR-410, JEOL NMR 500Λ or Bruker NMR AVANCE-600, Shimadzu GC-MS 17A, and JASCO V-550 spectrometers, respectively. The ^{13}C solid state NMR spectrum was recorded on a JEOL CMX-400. The molecular weight of the polymers was estimated by GPC (polystyrene gel column, eluent THF, polystyrene calibration).

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