Synthesis and Chemical Properties of Poly(*N*-substituted diphenylamine-4,4'-diyl)s

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A series of poly(diphenylamine)s with substituents at the *N*-position, $(\text{C}_6\text{H}_4\text{-}p\text{-NR-C}_6\text{H}_4\text{-}p)_n$ (*R* = methyl, butyl, hexyl, and benzoyl), were prepared by organometallic polycondensation using a zerovalent nickel complex. These polymers were soluble in organic solvents such as THF, *N*-methylpyrrolidone (NMP), and trifluoroacetic acid (TFA), and gave intrinsic viscosity of 0.52–0.93 dL g⁻¹. They showed number average molecular weights (M_n) of 3400–6100 with M_w/M_n (M_w = weight average molecular weight) of 1.9–2.4 in GPC analysis. The polymers exhibited photoluminescence (PL) with emission peaks at λ_{EM} = 408–425 nm in NMP solutions.

KEY WORDS: Poly(diphenylamine) / Organometallic Polycondensation / Conductivity / Optical Properties /

Much attention has been paid for polymers with electronic and optical functionalities. Poly(aniline)s^{1–8} are representative conducting polymers, and many papers have been reported for applications of the polymers. Their applications to electrodes of batteries,^{2a–c} anti-static materials,^{2d,e} active materials in electrochromic displays,³ and corrosion inhibitors⁴ have been carried out. Previously, we reported synthesis of poly(diphenylamine-4,4'-diyl) (**P(DPA)-Ni**) by organometallic polycondensation of 4,4'-dibrominated diphenylamine (DPA) using an Ni(0) complex, Ni(0)L_m,⁵ as a condensing agent.

P(DPA)-Ni had chemical properties different from those of **P(DPA)-Ox**, which was prepared by oxidative polymerization of $\text{C}_6\text{H}_5\text{NHC}_6\text{H}_5$.^{6a} **P(DPA)-Ni** is considered to have a well-defined linear structure shown in eq 1, because the Ni(0)L_m promoted polycondensation occurs selectively at the C-Br bond.^{5c} On the other hand, **P(DPA)-Ox** seems to contain structural irregularities because the oxidative polymerization can take place at various C-H positions of the phenyl group and at the NH group. **P(DPA)-Ox** was considered to contain at least two isomeric units, $-\text{C}_6\text{H}_4\text{-NH-C}_6\text{H}_4-$ and $-\text{C}_6\text{H}_4\text{-N(C}_6\text{H}_5)-$, in the polymer main chain.^{6e}

Oxidative polymerization of *N*-substituted diphenylamine has also been reported,^{6a–d,7,8c} and basic chemical properties of the obtained **P(N-R-DPA)-Ox** have been reported. However, synthesis of *N*-substituted diphenylamine *via* organometallic polycondensation has received less attention. **P(N-R-DPA)-Ox** is usually obtained in a p-doped oxidized state and some chemical treatment is usually needed to yield the polymer in a

neutral state. By contrast, the organometallic polycondensation gives the polymer (*e.g.*, **P(N-R-DPA)-Ni** by using Ni(0)L_m) in a neutral state, and studies of the polymer obtained by organometallic polycondensation are considered to be intriguing. The intrinsically neutral **P(N-R-DPA)-Ni** would be a useful material for electronic and optical applications (*e.g.*, as a hole-transporting material in organic light emitting diodes). In this paper, we report preparation of polymers of diphenylamines, $(\text{C}_6\text{H}_4\text{-}p\text{-NR-C}_6\text{H}_4\text{-}p)_n$, with the alkyl or benzoyl substituents (*R*) at the *N*-position *via* organometallic polycondensation similar to that expressed by eq 1. The obtained polymers showed high solubility in organic solvents and high thermal stability in TGA analysis.

EXPERIMENTAL

Materials and Measurements

¹H NMR and IR spectra were recorded on a JEOL FX-100 or EX-400 spectrometer and a JASCO IR 810 spectrophotometer, respectively. UV-vis and photoluminescence (PL) spectra were measured with a JASCO Ubest-35 spectrometer and a Hitachi F-4010 spectrophotometer, respectively. Elemental analysis was carried out by the Center for Advanced Materials Analysis (Suzukakedai) in Tokyo Institute of Technology. Molecular weight measurement was carried out with a Toso HLC-810 gel permeation chromatograph (eluent = DMF; polystyrene standards). Intrinsic viscosity was measured in NMP with an Ubbelohde viscometer at 30 °C. Thermal analysis was performed with a Shimadzu TA-50 WS thermal analyzer equipped with a Shimadzu DSC-50 differential scanning calorimeter and a Shimadzu TGA-50 thermogravimetric analyzer. Conductivity measurement was carried out by a two-probe method using a Sanwa CDS-820 digital multimeter. Iodine doping was carried out by exposure of a polymer powder to the vapor of iodine in a vacuum line. Excess iodine was removed under vacuum. The powder was collected by

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filtration and dried under vacuum. These doped samples were pressed into pellets at about 2×10^8 Pa. From the pellet, a bar is obtained by cutting the pellet, and carbon paste was put at both ends of the bar to measure the electrical conductivity. Bis(1,5-cyclooctadiene)nickel(0), $[\text{Ni}(\text{cod})_2]$,⁹ 4,4'-dibromodiphenylamine (**DPA-Br₂**),¹⁰ and *N*-hexyl-4,4'-dibromodiphenylamine (**N-Hex-DPA-Br₂**)^{7b} were prepared according to the literature.

Synthesis of Monomers

Synthesis of *N*-methyl-4,4'-dibromodiphenylamine (**N-Me-DPA-Br₂**). **N-Me-DPA-Br₂** was prepared by bromination of methyl-diphenylamine in a way analogous to that applied for the preparation of **DPA-Br₂**;¹⁰ Anal. Calcd for $\text{C}_{13}\text{H}_{11}\text{Br}_2\text{N}$: C, 45.8; H, 3.3; N, 4.1%. Found: C, 46.2; H, 3.1; N, 4.2%. IR (KBr): 3025, 2921, 1599, 1490, 1362, 1247, 1182, 814, 799 cm^{-1} . ¹H NMR (CDCl_3): δ 6.8–7.4 (m, aromatic, 8H), 3.25 (s, NCH_3 , 3H). UV-vis (CHCl_3): λ_{max} = 297 nm.

Synthesis of *N*-butyl-4,4'-dibromodiphenylamine (**N-Bu-DPA-Br₂**). To a THF-1,4-dioxane (1:1 v/v, 300 mL) mixed solution containing dispersed sodium hydride (0.684 g, 17.1 mmol) was added a THF solution (5 mL) of 4,4'-dibromodiphenylamine (5 g, 15.3 mmol) and 1-bromobutane (2.9 g, 21.4 mmol). The solution was refluxed for 12 h, and then cooled to room temperature. The volatile materials were removed under vacuum, and CHCl_3 (50 mL) and water (50 mL) were added to the residue. The organic phase was separated and washed with an aqueous solution of sodium carbonate (100 mL). After removal of the solvent by evaporation, the crude product was purified by column chromatography on SiO_2 (eluent = 1:1 mixture of hexane and ethyl acetate) and dried under vacuum to give **N-Bu-DPA-Br₂** as a colorless oil (64%). Anal. Calcd for $\text{C}_{16}\text{H}_{17}\text{Br}_2\text{N}$: C, 50.2; H, 4.5; N, 3.7%. Found: C, 50.8; H, 4.8; N, 3.4%. IR (KBr): 3025, 2920, 2854, 1599, 1490, 1362, 1247, 1182, 814, 799 cm^{-1} . ¹H NMR (CDCl_3): δ 7.36–6.84 (m, aromatic, 8H), 3.68 (t, NCH_2 , 2H), 1.7–1.4 (m, $\text{N}(\text{CH}_2)_2$, 2H), 0.92 (t, CH_3 , 3H). UV-vis (CHCl_3): λ_{max} = 305 nm.^{5d} Similar synthesis of **N-Bu-DPA-Br₂** has been reported.^{6a}

Synthesis of *N*-benzoyl-4,4'-dibromodiphenylamine (**N-Bz-DPA-Br₂**). **N-Bz-DPA-Br₂** was prepared analogously from **DPA-Br₂** and PhCOCl ; Yield, 77%. Anal. Calcd for $\text{C}_{19}\text{H}_{13}\text{Br}_2\text{NO}$: C, 52.9; H, 3.0; N, 3.3%. Found: C, 53.1; H, 3.1; N, 3.3%. IR (KBr): 3053, 1653, 1562, 1481, 1396, 1322, 1290, 1101, 1063, 1006, 810, 778 cm^{-1} . ¹H NMR (CDCl_3): δ 7.5–6.9 (m, aromatic, 13H). UV-vis (CHCl_3): λ_{max} = 256 nm.

Synthesis of Polymers

Poly(*N*-methyl-diphenylamine-4,4'-diyl) (P(*N*-Me-DPA)-Ni). To a dry DMF solution (25 mL) of $\text{Ni}(\text{cod})_2$ (1.93 g, 7.03 mmol), 1,5-cyclooctadiene (1.5 mL), and 2,2'-bipyridyl (1.10 g, 7.03 mmol) was added **N-Me-DPA-Br₂** (2.0 g, 5.86 mmol), and the mixture was stirred at 60 °C. After 16 h, the reaction mixture was poured into an aqueous solution of ammonia. The yellow-green powder was collected by filtration, and washed with diluted hydrochloric acid, a warm aqueous solution of disodium ethylenediaminetetraacetate (Na_2EDTA), diluted aqueous am-

monia, water, and methanol successively. Drying the remaining powder under vacuum for 24 h gave **P(*N*-Me-DPA)-Ni** in 87% yield. Removal of by-products (e.g., Ni compounds) by washing was accomplished rather easily and an ash-free polymer was obtained. Anal. Calcd for $[\text{C}_{13}\text{H}_{11}\text{N} \cdot (\text{H}_2\text{O})_{0.3}]_n$: C, 83.7; H, 6.3; N, 7.5%. Found: C, 83.5; H, 6.2; N, 7.6; Br, 0; ash, 0%. IR (KBr): 3018, 2890, 2842, 1596, 1498, 1345, 1246, 1172, 822, 791 cm^{-1} . ¹H NMR ($\text{CF}_3\text{CO}_2\text{D}$, 400 MHz): δ 7.6–7.1 (m, aromatic, 8H), 3.38 (s, NCH_3 , 3H). ¹³C{¹H} NMR ($\text{CF}_3\text{CO}_2\text{D}$, 100 MHz): δ 146.2, 142.1, 130.4, 122.8, 63.5. UV-vis (NMP): λ_{max} = 347 nm.

Poly(*N*-butyldiphenylamine-4,4'-diyl) (P(*N*-Bu-DPA)-Ni). **P(*N*-Bu-DPA)-Ni** was prepared analogously; Yield, 82%. Anal. Calcd for $[\text{C}_{16}\text{H}_{17}\text{N} \cdot (\text{H}_2\text{O})_{0.2}]_n$: C, 84.7; H, 7.7; N, 6.2%. Found: C, 84.8; H, 7.5; N, 6.2; Br, 0; ash, 0%. IR (KBr): 3028, 2920, 2854, 1599, 1490, 1362, 1247, 1182, 814, 799 cm^{-1} . ¹H NMR (CDCl_3 , 400 MHz): δ 7.5–7.0 (m, aromatic, 8H), 3.76 (t, NCH_2 , 2H), 1.7–1.2 (m, $\text{NCH}_2(\text{CH}_2)_2$, 4H), 0.96 (t, CH_3 , 3H). ¹³C{¹H} NMR ($\text{CF}_3\text{CO}_2\text{D}$, 100 MHz): δ 146.7, 133.5, 127.3, 121.1, 52.2, 29.7, 20.3, 13.9. UV-vis (NMP): λ_{max} = 358 nm.

Poly(*N*-hexyldiphenylamine-4,4'-diyl) (P(*N*-Hex-DPA)-Ni). **P(*N*-Hex-DPA)-Ni** was prepared in an analogous way; Yield, 88%. Anal. Calcd for $[\text{C}_{18}\text{H}_{21}\text{N} \cdot (\text{H}_2\text{O})_{0.2}]_n$: C, 84.8; H, 8.5; N, 5.5%. Found: C, 84.7; H, 8.5; N, 5.5; Br, 0; ash, 0%. IR (KBr): 3028, 2920, 2854, 1599, 1490, 1362, 1247, 1182, 814, 799 cm^{-1} . ¹H NMR ($\text{CF}_3\text{CO}_2\text{D}$, 400 MHz): δ 7.92–7.74 (m, aromatic, 8H), 4.36 (t, NCH_2 , 2H), 1.86 (m, NCH_2CH_2 , 2H), 1.53 (m, $\text{NCH}_2\text{CH}_2\text{CH}_2$, 2H), 1.42 (m, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2$, 4H), 0.95 (t, CH_3 , 3H). ¹³C{¹H} NMR ($\text{CF}_3\text{CO}_2\text{D}$, 100 MHz): δ 143.5, 141.9, 131.1, 123.5, 61.6, 31.9, 26.7, 23.0, 13.3. UV-vis (NMP): λ_{max} = 366 nm.

Poly(*N*-benzoyldiphenylamine-4,4'-diyl) (P(*N*-Bz-DPA)-Ni). **P(*N*-Bz-DPA)-Ni** was prepared in an analogous way; Yield, 98%. Anal. Calcd for $[\text{C}_{19}\text{H}_{13}\text{NO} \cdot (\text{H}_2\text{O})_{0.4}]_n$: C, 81.9; H, 5.0; N, 5.0%. Found: C, 81.8; H, 4.8; N, 5.2; Br, 0; ash, 0%. IR (KBr): 3031, 1658, 1599, 1491, 1331, 1298, 1012, 817, 782 cm^{-1} . ¹H NMR ($\text{CF}_3\text{CO}_2\text{D}$, 400 MHz): δ 7.8–7.3 (m, aromatic, 13H). ¹³C{¹H} NMR ($\text{CF}_3\text{CO}_2\text{D}$, 100 MHz): δ 177.4, 143.5, 142.3, 133.6, 130.7, 130.3, 129.7, 129.2, 128.3. UV-vis (NMP): λ_{max} = 310 nm.

RESULTS AND DISCUSSION

Polymer Synthesis

Dehalogenative polycondensation of **N-R-DPA-Br₂** using the Ni(0) complex gave the corresponding poly(*N*-substituted diphenylamine-4,4'-diyl) (**P(*N*-R-DPA)-Ni**), as shown in Scheme 1. The polymers were obtained as a yellow powder in good yields (82–98%), and they were worked-up by washing with an aqueous solution of Na_2EDTA to remove Ni compounds. Table I summarizes the results of polymerization. The data from elemental analysis of the polymers agreed with partially hydrated (e.g., 0.2 H_2O per the repeating unit) polymers. The $-\text{C}_6\text{H}_4-p-\text{N}(\text{R})-\text{C}_6\text{H}_4-p-$ unit is considered to be intact during the polymerization even for the benzoyl-

Scheme 1. Preparation of **P(N-R-DPA)-Ni**.**Table I.** Results of preparation of **P(N-R-DPA)-Nis**^a

Polymer	yield/%	<i>M_n</i> ^b	<i>M_w</i> ^b	<i>M_w/M_n</i> ^b	[<i>η</i>] ^c /dL g ⁻¹
P(DPA)-Ni ^d	97	6400	20000	3.13	0.66
P(N-Me-DPA)-Ni	87	6100	14500	2.37	0.52
P(N-Bu-DPA)-Ni	82	5700	12000	2.11	0.74
P(N-Hex-DPA)-Ni	88	5400	10090	1.87	0.93
P(N-Bz-DPA)-Ni	98	3400	8200	2.41	0.62

^aPolymerization was carried out in DMF at 60 °C for 16 h. ^bDetermined by GPC (polystyrene standard; eluent = a 0.01 M LiBr/DMF solution).

^cIntrinsic viscosity measured in NMP at 30 °C. ^dFrom ref 5b.

substituted unit. Detection of no Br suggested that the formed polymer contained a polymer-Ni terminal groups as the major terminal group, and the polymer-Ni group was converted to a polymer-H group during work-up, similar to cases of poly-(heterocycles) prepared analogously.¹¹

The relatively large [*η*] for *M_n* of the polymers (*cf.* Table I) suggested a stiff structure of the polymers. **P(N-R-DPA)-Nis** showed comparable or higher solubility than that of **P(DPA)-Ni** as shown in Table II. The Bu and Bz polymers were soluble in CHCl₃, whereas **P(DPA)-Ni** was not soluble in CHCl₃. **P(DPA)-Ox** prepared by oxidative polymerization using diphenylamine or 4-aminobiphenyl did not have good solubility in organic solvents.^{6c} **P(N-R-DPA)-Oxs** in a BF₄-doped state were also soluble in organic solvents.^{6b}

Figure 1 shows comparison of IR spectra of **P(N-R-DPA)-Nis** with that of **P(DPA)-Ni**. The ν(N-H) peak of **P(DPA)-Ni** at 3388 cm⁻¹ reasonably disappears in the IR spectra of **P(N-R-DPA)-Nis**. **P(N-Bz-DPA)-Ni** gives rise to a strong ν(C=O) peak at 1658 cm⁻¹. All the polymers show an IR peak at about

Figure 1. IR spectra of **P(DPA)-Ni** (from ref. 5b), (a) **P(N-Me-DPA)-Ni**, (b) **P(N-Bu-DPA)-Ni**, (c) **P(N-Hex-DPA)-Ni**, and (d) **P(N-Bz-DPA)-Ni**.

800 cm⁻¹, which is assigned to a δ(C-H) peak of the *p*-phenylene unit.^{1,8c}

NMR data of the polymers also agreed with the polymer structures. Figure 2 displays ¹H and ¹³C{¹H} NMR spectra of **P(N-Hex-DPA)-Ni** in CF₃CO₂D. In the ¹H NMR spectrum of

Table II. Solubility of **P(N-R-DPA)-Nis**

solvent	P(N-Me-DPA)-Ni	P(N-Bu-DPA)-Ni	P(N-Hex-DPA)-Ni	P(N-Bz-DPA)-Ni	P(DPA)-Ni ^a
NMP	S	S	S	S	S
DMF	PS	S	S	PS	PS
acetone	I	I	I	I	I
HCO ₂ H	I	PS	PS	I	I
CF ₃ CO ₂ H	S	S	S	S	S
THF	PS	S	S	S	PS
hexane	I	I	I	I	I
toluene	I	I	I	I	I
DMSO	PS	PS	PS	PS	PS
CHCl ₃	I	S	S	S	I
MeOH	I	I	I	I	I
CH ₃ CN	I	I	I	I	I

S: Soluble, PS: Partially soluble, I: Insoluble. ^aFrom ref 5b.

Figure 2. ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of **P(N-Hex-DPA)-Ni** in $\text{CF}_3\text{CO}_2\text{D}$.

P(N-Hex-DPA)-Ni, an AB quartet pattern of *p*-phenylene unit centered at δ 7.84 is observed. The signals of the hexyl group are exhibited at δ 4.36, 1.86, 1.53, 1.42, and 0.95, and the peak area ratio between the aromatic signals and the aliphatic signals agrees well with the structure of **P(N-Hex-DPA)-Ni**. As shown in Figure 2b, the $^{13}\text{C}\{^1\text{H}\}$ NMR of **P(N-Hex-DPA)-Ni** shows sharp four peaks of the *p*-phenylene group at δ 123.5, 131.1, 141.9, and 143.5, and the hexyl signals are observed at δ 13.3, 23.0, 26.7, 31.9, and 61.6. Other **P(N-R-DPA)-Nis** also gave reasonable IR and NMR data, indicating that they had a linear main chain with well-defined bonding between the monomeric units. The $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of **P(N-R-DPA)-Nis** are similar to reported $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of **P(N-R-DPA)-Oxs**,^{6a,8c} revealing that **P(N-R-DPA)-Oxs** also have essentially linear structure as **P(N-R-DPA)-Nis**. ^1H NMR spectra of **P(N-R-DPA)-Oxs** have not been reported to our best knowledge.

Chemical Properties

Thermogravimetric analysis (TGA) data of **P(N-R-DPA)-Nis** are shown in Figure 3. Weight loss of the polymer starts at about 400 °C with 15–48% residual weight at 900 °C under N_2 . The weight loss starting temperatures were lower than that of **P(DPA)-Ni** (about 500 °C),^{5b} however, the polymers still had high thermal stability.

Figure 3. TGA traces of (a) **P(N-Me-DPA)-Ni**, (b) **P(N-Bu-DPA)-Ni**, (c) **P(N-Hex-DPA)-Ni**, and (d) **P(N-Bz-DPA)-Ni**.

Figure 4. UV-vis spectra of (a) **P(N-Me-DPA)-Ni**, (b) **P(N-Bu-DPA)-Ni**, (c) **P(N-Hex-DPA)-Ni**, and (d) **P(N-Bz-DPA)-Ni** in NMP.

Table III. Optical data of polymers

Polymer	UV-vis ($\lambda_{\text{max}}/\text{nm}$) ^a	PL ($\lambda_{\text{EM}}/\text{nm}$) ^a
P(DPA)-Ni ^b	380	417, 440sh
P(N-Me-DPA)-Ni	347	408, 432sh
P(N-Bu-DPA)-Ni	358	414, 436sh
P(N-Hex-DPA)-Ni	366	425, 449sh
P(N-Bz-DPA)-Ni	310	412, 430sh

^aSolvent = NMP. sh: shoulder peak. ^bFrom ref 5b.

Figure 4 shows UV-vis spectra of **P(N-R-DPA)-Nis** in NMP. Optical data of the polymers are summarized in Table III. The π – π^* absorption peaks of the polymers appear at $\lambda_{\text{max}} = 347$ –366 nm for **P(N-alkyl-DPA)-Ni** and 310 nm for **P(N-Bz-DPA)-Ni**, respectively. The peak positions are shifted to a longer wavelength by 51–53 nm from those of the corresponding monomers, $\text{Br-C}_6\text{H}_4$ –*p*– NR – C_6H_4 –*p*– Br . The UV-vis data of **P(N-R-DPA)-Ni** essentially agree with that of **P(N-R-DPA)-Ox**,^{6a,b} indicating that the latter polymer is essentially completely dedoped during work-up. **P(DPA)-Ni** showed the absorption peak at a somewhat longer wavelength, $\lambda_{\text{max}} = 380$ nm.^{5b} It is reported that electronic interaction between aromatic rings *via* the –NR– group is possible and the electronic interaction decreases when a sterically large R group is attached at N.^{8c,d}

Figure 5. PL (solid line) and excitation (dashed line) spectra of **P(N-Hex-DPA)-Ni** in NMP.

Figure 5 discloses PL and excitation spectra of **P(N-Hex-DPA)-Ni** in NMP. **P(N-Hex-DPA)-Ni** emits blue colour in PL and shows the PL peak at $\lambda_{\text{EM}} = 425$ nm with a shoulder peak at $\lambda_{\text{EM}} = 449$ nm. The λ_{EM} position agrees with the onset position of the UV-vis absorption band. Monitoring PL at 425 and 449 nm gave essentially the same excitation spectra. Other polymers were also luminescent and showed λ_{EM} in a range of 408–425 nm (Table III). These λ_{EM} values are comparable to those of **P(DPA)-Ni** ($\lambda_{\text{EM}} = 417$ nm)^{5b} and analogous dipyrrolyl amine polymers, $(\text{C}_5\text{H}_3\text{N-NR-C}_5\text{H}_3\text{N})_n$ ($\lambda_{\text{EM}} = 415$ nm for R = hexyl and 416 nm for R = (S)-2-methylbutyl).^{8c} **P(N-R-DPA)-Nis** themselves were insulating materials with electrical conductivity (σ) below 10^{-9} S cm⁻¹. After exposure of the polymers to an I₂ vapor, the Me, Bu, Hex, and Bz polymers showed electrical conductivity of 2.0×10^{-2} , 2.4×10^{-3} , 1.7×10^{-3} , and 3.3×10^{-4} S cm⁻¹, respectively.

CONCLUSION

New alkyl derivatives of poly(diphenylamine), **P(N-R-DPA)-Nis**, were prepared and characterized by IR, ¹H and ¹³C{¹H} NMR, and elemental analysis. The polymers, especially the Bu and Hex polymers, had good solubility in organic solvents, and gave M_n values of 3400–6100 with $M_w/M_n = 1.9$ –2.4 and $[\eta]$ values of 0.52–0.93 dL g⁻¹. They showed good thermal stability. UV-vis data suggested expansion of the electronic system through the -N(R)- group and they showed PL peaks at about 420 nm.

Received: April 22, 2009

Accepted: June 13, 2009

Published: July 29, 2009

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