Synthesis and characterization of an oligomeric conjugated metal-containing poly(*p*-phenylenevinylene) analogue†

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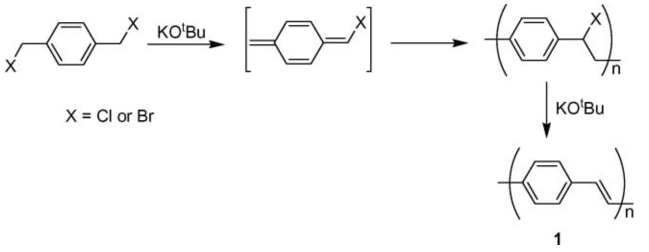
A new nickel-containing bis(bromobenzyl)salphen monomer suitable for Gilch polymerization was prepared. Reaction with KO^{t}Bu in THF–DMF afforded primarily gels, but also soluble, conjugated oligomers that are red-shifted in the absorption spectrum when compared to the monomer. This spectral change, consistent with an enhanced conjugation length, was also compared with a suitable model compound for the polymer. Our results indicate that Gilch polymerization may be a useful route to fully conjugated metal-containing polymers if attention is paid to ensuring solubility of the product.

Introduction

Conjugated polymers have been the subject of intense research since the discovery in 1977 that doped polyacetylene is metallic.[1] The conjugation in these organic materials is facilitated by unsaturated bonding within the backbone that enables delocalization of electrons within the π-orbitals, and gives rise to a band structure. In general, the conjugation in organic polymers is limited by defects and rotation of bonds within the backbone. By preventing the rotation of the components in the conjugated polymer, the conjugation may be extended, improving the extent of exciton delocalization and charge carrier migration.[2] Efforts to hinder rotation have included using conjugated and saturated linkers between segments of the backbone.[3] Metal complexation may be used to modify the conjugation by hindering rotation of the polymer. For example, Swager and coworkers have used this mechanism to inhibit the conjugation in polythiophene segments, leading to measurable property changes that can be used in sensing.[4]

There is a growing interest in the synthesis and characterization of metal-containing conjugated polymers due to their potential in materials science.[5,6] In addition to affecting the conformation of the polymer, the introduction of a metal center into the conjugated polymer chain may produce a range of characteristics that differ from those of conventional organic polymers, *e.g.* redox, magnetic, optical and electronic properties.[7] Incorporation of chromophores, such as Schiff-base complexes,[8] into polymers has been investigated for developing catalysts[9] and luminescent materials for potential application in light-emitting diodes (LEDs).[10] Schiff-base complexes incorporated into polymers *via* electropolymerization offer binding sites for the 4-electron reduction of oxygen to water.[11] We have reported conjugated poly(*p*-phenyleneethynylene)s that incorporate Schiff-base complexes of Ni^{2+}, VO^{2+}, Zn^{2+}, and Cu^{2+}.[12] The metal complexes strongly influence the optical properties of the conjugated polymer. Although intractable conjugated polymers containing Schiff-base complexes in the backbone are known, we were able to ensure solubility with the use of long alkyl substituents. The dearth of viable synthetic routes to conjugated metal-containing polymers, as well as the difficulty of producing soluble polymers has impeded progress in this field.

Since the discovery of electroluminescence in poly(*p*-phenylenevinylene) (PPV, **1**) in 1990,[13] many derivatives of PPV have been prepared, particularly for application in light-emitting diodes (LEDs).[14,15] PPV derivatives with bulky alkoxy side groups have been most extensively studied as these substituents enhance both solubility and quantum efficiency.[16] Various approaches to synthesize soluble dialkoxy PPVs have been reported in the literature including the Gilch route,[17] the Wittig reaction,[18] and aryl-ethylene coupling *via* Heck or Suzuki reactions.[19] Among these methods, the Gilch route is commonly used because it is a simple one-pot process. In the Gilch polymerization route, a 1,4-di(halogenomethyl)benzene structure is postulated to undergo an elimination reaction to form a quinodimethane intermediate that polymerizes, as shown in Scheme 1.[20] In a second step, elimination of HX affords the conjugated PPV. Most research based on the synthesis of PPV by the Gilch route has focused on changing the functional groups on the monomer precursor in order to form the quinodimethane intermediate more readily. A few papers have reported the synthesis of poly(fluorenevinylene) derivatives by Gilch polymerization in which electrons transfer over four double bonds to give the quinodimethane intermediate.[21] We are aware of only two papers that show a more complicated system, in which researchers attempted to incorporate porphyrin units[22] and 1,3,4-oxadiazole segments[23] into the copolymer backbone. These copolymers contained less than 2 mol% of porphyrin and less than



Scheme 1 Synthesis of PPV by the Gilch polymerization.

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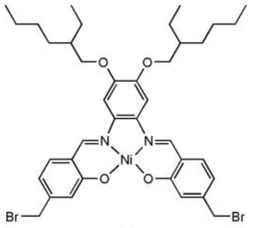
30% of oxadiazole segments. It was not possible to include larger quantities of porphyrin and oxadiazole into the polymer due to solubility limitations.

We report here the design and synthesis of a new Schiff-base metal complex that functions as a monomer for the preparation of a metal-containing PPV analogue. The synthesis and characterization of the conjugated homopolymer, as well as a new conjugated model compound, are discussed. During the formation of the quinodimethane intermediate in our system, an elimination reaction over seven double bonds must occur.

Results and discussion

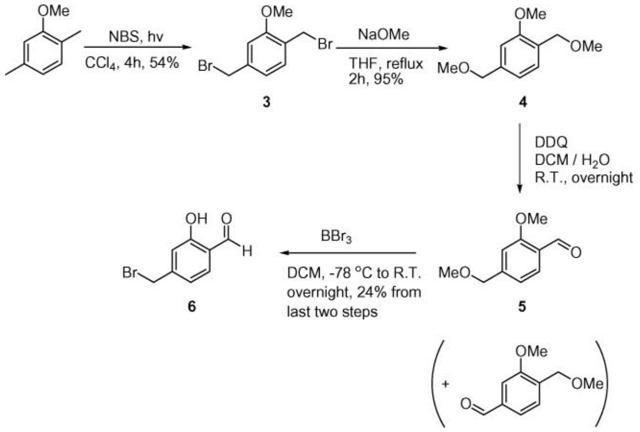
The best method to ensure complete metallation of a conjugated polymer is to polymerize the metal-containing monomer, rather than post-polymer modification. We proposed to synthesize a new monomer **2** containing two benzylbromide substituents as a possible precursor to a metallo-PPV analogue. This monomer features branched alkoxy groups with stereogenic centers for solubility and a square planar nickel(II) center to maintain planarity and, thus, conjugation in the monomer. In this monomer, the elimination reaction would extend over a distance of 16 atoms, as will be discussed.



2

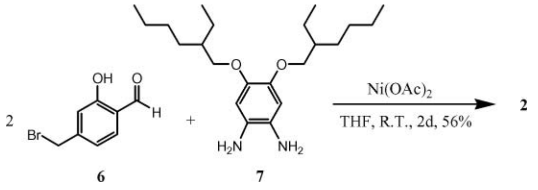
To synthesize monomer **2**, we required 4-bromomethyl-2-hydroxybenzaldehyde **6**, a previously unknown compound. Although 5-halomethyl-2-hydroxybenzaldehyde can be prepared easily by chloro- or bromomethylation of salicylaldehyde,[24] we knew it would be much more difficult to obtain the isomer we desired in **6**. There is one report of a related compound (4-chloromethyl-2-hydroxybenzaldehyde).[25]

Scheme 2 illustrates our route to compound **6**. 1,4-Bis(bromomethyl)anisole **3** was prepared *via* free-radical bromination of commercially available 2,5-dimethylanisole.[26] Compound **3** was then converted into 2,5-bis(methoxymethyl)anisole **4** in 95% yield upon treatment with excess NaOMe in THF.[27] Selective oxidation of compound **4** with 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) in 10 : 1 CH_2Cl_2–H_2O gave 2-methoxy-4-(methoxymethyl)benzaldehyde **5**.[27] In this reaction, the product obtained is a mixture of **5** and its isomer 3-methoxy-4-(methoxymethyl)benzaldehyde in a 5 : 1 ratio. As the separation of the isomers was difficult at this stage, the mixture was used for the next step without purification. In the final step, a simultaneous deprotection of the phenol as well as the benzyl methyl ether with BBr_3 gave the desired compound **6**. This product could be purified by flash chromatography on SiO_2 (in 1 : 2 DCM : hexanes) and stored in the fridge. The by-product was easily separated from the desired compound **6** by this method. It is noteworthy that compound **6** is relatively unstable; attempts to concentrate it by rotary evaporation at > 30–40 °C resulted in decomposition to a thick, brown paste with visible HBr production.



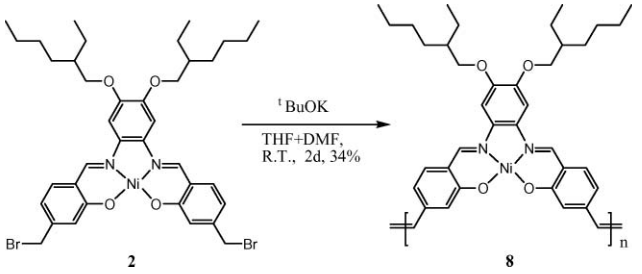
Scheme 2 Synthesis of compound **6**.

Schiff-base condensation of **6** with 4,5-diamino-1,2-bis(2-ethylhexyloxy)benzene **7** in the presence of nickel(II) acetate yielded monomer **2** in 56% yield, Scheme 3. The ^1H NMR spectrum of **2** was extremely broad in $CDCl_3$, suggesting strong aggregation that results in a decrease of the T_2 relaxation time for the protons. Upon addition of a trace of THF-d_8, sharp peaks were observed and could be assigned to the resonances of the protons expected for compound **2**. In particular, the imine resonance was observed at 7.78 ppm, and the resonance of the protons on the bromomethyl substituents was present as a singlet at 4.35 ppm. Other characterization was also consistent with the complex.



Scheme 3 Synthesis of nickel-containing monomer **2**.

Polymerization of **2** with an excess of ^tBuOK in a mixture of THF and DMF afforded the new polymer **8**, Scheme 4. The low yield was attributed to the formation of a gel that would not dissolve in any solvent we tried. Gelation is a common problem for Gilch polymerization reactions, but the source of its formation remains under discussion.[28] Our attempts to obtain polymer **8** were severely frustrated by gel formation. Researchers have published the polymerization procedure under many different conditions to overcome gelation, several of which we tried to optimize the preparation of polymer **8**.[29] Table 1 summarizes some of the



Scheme 4 Synthesis of Schiff base polymer **8**.

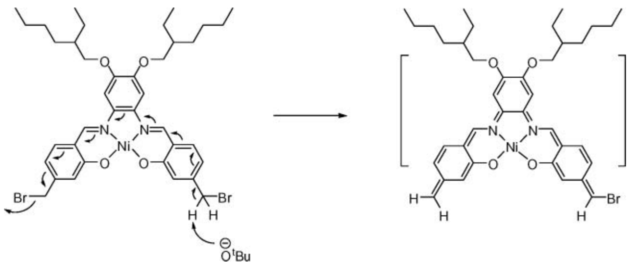
Table 1 Summary of conditions used for polymerization of **2**

Solvent	Reagents	T/°C	Yield[a]	M_n[b]
THF	^{t}BuOK	50	Gelation	—
THF	^{t}BuOK	20	10%	3300
THF	*tert*-Butylbenzylchloride + ^{t}BuOK	20	Gelation	—
THF	KOH + Bu_4NBr	0	Less than 5%	240
DMF	^{t}BuOK	50	Gelation	—
DMF	^{t}BuOK	20	73%	1000
THF + DMF	^{t}BuOK	20	34%	5560

[a] Yield of soluble fraction. [b] Measured by GPC (THF) relative to polystyrene standards

conditions we tried to obtain the soluble polymer. In general, most of the procedures afforded exclusively or primarily insoluble material. In an attempt to terminate the end groups with *p-tert*-butylbenzyl groups, *p-tert*-butylbenzylchloride was added to the reaction (entry #3), but still only insoluble material was obtained.

Typically, the elimination reaction in the first step of the Gilch polymerization proceeds over a single benzene ring as illustrated for PPV in Scheme 1. In the case of monomer **2**, the elimination reaction to afford a quinodimethane intermediate must occur through the entire structure. We rationalized that positioning the benzylic halide groups *para* to the imine groups on **2** would allow electron transfer through the entire ligand system to occur, giving a quinodimethane-like intermediate, as shown in Scheme 5.



Scheme 5 Proposed elimination step in monomer **2** to give the quinodimethane-like intermediate, which undergoes polymerization to form polymer **8**.

During the polymer preparation, we were concerned that ^{t}BuOK could react with the imine on the monomer, possibly destroying the complex during the reaction. Deprotonation of the imine functionality with ^{t}BuOK has been reported.[30] To test whether this was a problem, a simple nickel(II) salphen molecule was reacted under similar conditions to monomer **2** with excess ^{t}BuOK. After the experiment, the reaction was quenched with methanol and the product was analyzed. NMR spectroscopy indicated that the complex was stable, though it is possible that the monomer was deprotonated during the polymerization reaction, and this could be one cause of the gel formation.

Based on our experiments, we found that polymerization in a mixture of THF and DMF gave less gelation and higher molecular weight than in pure THF or DMF. The resulting red material is soluble in THF and DCM, and was characterized by gel permeation chromatography (GPC), elemental analysis, and thermogravimetric analysis (TGA), as well as by UV-vis, IR, and NMR spectroscopies.

GPC of the polymer (see ESI†) indicated that the highest molecular weight fractions had a molecular weight of only *ca.* 5600 Da (M_n), indicating that the oligomer contains only 7–8 repeat units in its structure. Nevertheless, this is still respectable for conjugated metallopolymers, which are rarely soluble and generally synthesized in low molecular weights. The required electron transfer/elimination reaction through the entire ligand during the polymerization may also inhibit polymerization and prevent the generation of high molecular weight polymer. Elemental analysis was also consistent with *ca.* 3–4 repeat units in the polymer, assuming terminal CH_2Br substituents. We have found that elemental analysis of our metal-containing polymers often underestimates the amount of carbon present in the polymer, possibly due to coordination of water.

TGA of the product showed decomposition at 250 °C, more than 50 °C higher than for the monomer. The char that remained (11.4 mass%) corresponds to the expected mass if the product is primarily NiO.

Comparison of the IR spectra obtained from the polymer and the monomer confirms that the Schiff-base complex is still intact in the polymer. The C=N vibration appears at 1602 cm^{-1} in the polymer. A peak at 1275 cm^{-1} is attributed to the C–O stretching vibration of the phenol structure. The two bands near 530 cm^{-1} and 455 cm^{-1} belong to the vibration of Ni–O and Ni–N, respectively. Importantly, a new peak appears at 1695 cm^{-1} in the IR spectrum of the polymer, Fig. 1. This medium strength band is assigned to the C=C stretching vibration of PPV chains. The band observed in the both monomer and compound **6** at 669 cm^{-1}, which is assigned to the C–Br stretch vibration, is absent in the IR spectrum of **8**.

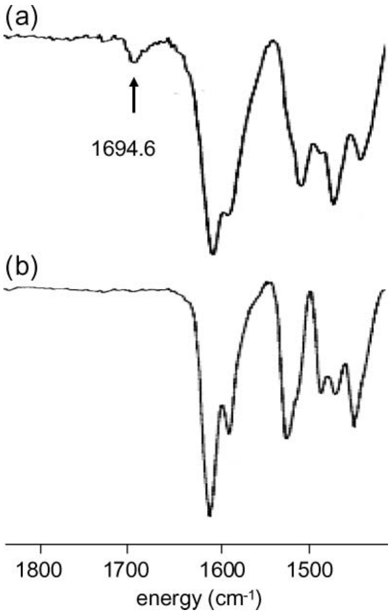
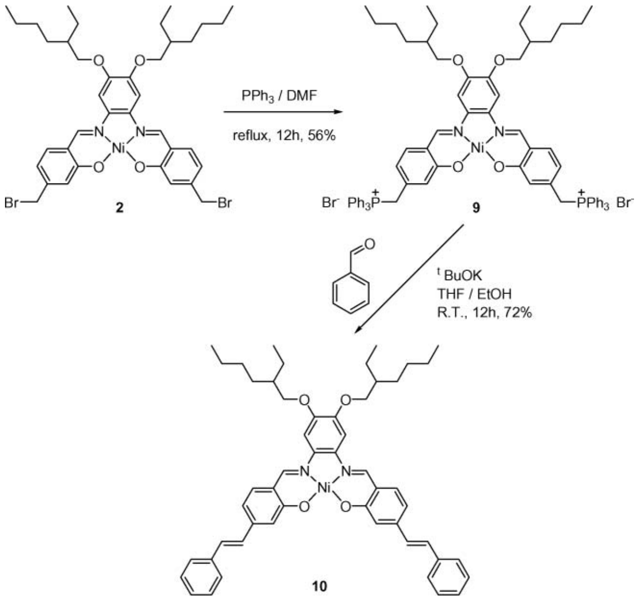


Fig. 1 IR spectra of (a) polymer **8** and (b) monomer **2** between 1400–1800 cm^{-1}, showing the C=C stretching mode at 1695 cm^{-1} in the polymer.

The ^1H NMR spectrum of **8** is very broad, suggestive of aggregation, and unlike the spectrum for **2**, the spectrum for **8** does not become sharp upon addition of coordinating solvents. The ^1H NMR spectrum of the polymer in CD_2Cl_2 (with a trace of THF-d_8) is consistent with the proposed polymer structure and indicates the absence of residual monomer or short oligomers that would be expected to show sharp resonances. A broad peak at 7.6–8.0 ppm is assigned to the imine resonance. A broad peak between 6 and 7.5 ppm is attributed to the protons of aromatic and ethenyl groups. There is also a small peak at 3.9 ppm assigned to protons on OCH_2. We could not observe a peak near 4.35 ppm where the CH_2Br peak in monomer **2** was located, but it may be very weak if only due to end groups in the polymer. The aggregation of the polymer prevented us from obtaining useful ^{13}C NMR data.

To provide further confirmation of the polymer structure, we prepared model compound **10** as shown in Scheme 6. Treatment of monomer **2** with triphenylphosphine in DMF afforded the Wittig reagent **9**. ^1H, ^{13}C, and ^{31}P NMR and MS data for this compound were consistent with its structure. Condensation with benzaldehyde gave the distilbene model compound **10** in 72% yield. NMR and MS data for this compound were in agreement with its structure.



Scheme 6 Synthesis of model compound **10**.

Fig. 2 displays the UV-vis spectra of homopolymer **8**, together with the spectra of monomer **2** and model compound **10**. Compared to the spectrum of monomer **2**, the UV-vis absorption spectrum of **8** was broader and slightly red-shifted, consistent with extended conjugation. The bandgaps calculated from UV-vis are 2.0 eV and 2.2 eV for the polymer and the monomer, respectively. Overall, the features in the visible region of the spectrum are similar for the monomer, the polymer, and the model compound. These are quite likely dominated by charge-transfer bands within the complex.

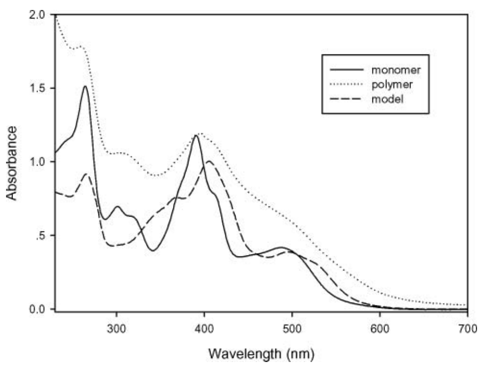


Fig. 2 UV-vis spectra (1.0 cm cell, 298 K, THF) of monomer **2**, polymer **8**, and model compound **10** in THF.

Experimental

2,5-Dimethylanisole, sodium methoxide (25% in methanol), N-bromosuccinimide (NBS), 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ), boron tribromide (BBr_3), nickel(II) acetate, and triphenylphosphine (PPh_3) were obtained from Aldrich. Deuterated solvents were obtained from Cambridge Isotope Laboratories, Inc. Tetrahydrofuran was distilled from sodium/benzophenone under N_2. 2,5-Di(bromomethyl)anisole (**3**),[26] 2-methoxy-4-(methoxymethyl)benzaldehyde (**4**),[27] and 4,5-diethylhexyloxy-1,2-phenylenediamine [31] were prepared by literature methods.

All reactions were carried out under a nitrogen atmosphere using Schlenk techniques or in a N_2 glovebox (MBraun) unless otherwise noted. ^1H and ^{13}C NMR spectra were recorded on Bruker AV-400 and AV-300 spectrometers. ^{13}C NMR spectra were recorded using a proton decoupled pulse sequence. UV-Vis spectra were obtained in distilled THF on a Varian Cary 5000 UV-Vis/near-IR spectrometer using a 1 cm quartz cuvette. IR spectra were obtained as neat in the solid state on a Thermo Nicolet 6700 FT-IR spectrometer. Molecular weights were estimated by gel permeation chromatography (GPC) in THF using a Waters liquid chromatograph. Narrow molecular weight polystyrene standards were used for calibration purposes. Electrospray (ESI) mass spectra were obtained at the UBC Microanalytical Services Laboratory on a Micromass LCT time-of-flight (TOF) mass spectrometer equipped with an electrospray ion source. MALDI-TOF mass spectra were obtained in a dithranol matrix (cast from THF) on a Brüker Biflex IV instrument where spectra were acquired in the positive reflection mode with delay extraction. Melting points were obtained on a Fisher-John's melting point apparatus.

Synthesis of 2-hydroxy-4-(bromomethyl)benzaldehyde 6

To a mixture of 1 g (3.4 mmol) of 2,5-di(methoxymethyl)anisole (**4**) in 300 mL of 10 : 1 dichloromethane–water was added 1.15 g (5.0 mmol) of DDQ and the reaction mixture was vigorously stirred at room temperature overnight. The red mixture was then poured into saturated sodium bicarbonate and stirred for 30 min. After the mixture separated, the aqueous layer was extracted with dichloromethane (3 × 50 mL). The combined organic fractions were washed with brine then water, and dried over $MgSO_4$. After filtration and concentration by rotary evaporation, the crude product was used for the next step without further purification. ^1H NMR spectroscopy indicated that the product was a mixture of 2-methoxy-4-(methoxymethyl)benzaldehyde and 3-methoxy-4-(methoxymethyl)benzaldehyde, but the product was not easily separated at this stage.

Under an atmosphere of nitrogen the crude product from above was dissolved in 200 mL of anhydrous dichloromethane. The solution was cooled by dry ice/acetone and 1 mL of BBr_3

(10.4 mmol) was added. The red solution was stirred overnight allowing the reaction mixture to slowly warm to room temperature. After pouring the reaction onto ice, the product was extracted with dichloromethane (3 × 50 mL). The combined organic fractions were dried over $MgSO_4$, filtered, and dried by rotary evaporation. During rotary evaporation, the temperature of the water bath must be lower than 30 °C to prevent rapid decomposition. The crude yellow solid was purified by flash column chromatography on SiO_2 with DCM : hexanes = 1 : 2. Rotary evaporation of the solvent at low temperature afforded a yellow solid. The compound decomposes on standing at room temperature and must be stored in the fridge. Yield: 0.17 g (0.78 mmol, 24%) based on 2 steps. ^1H NMR($CDCl_3$): $\delta = 11.04$ (s, 1H), 9.87 (s, 1H), 7.55 (d, 1H), 7.02 (d, 1H), 6.99 (s, 1H), 4.40 (s, 2H) ppm. ^{13}C NMR ($CDCl_3$): $\delta = 196.1$, 161.9, 147.1, 134.4, 120.8, 120.5, 118.2, 31.9 ppm. EI-MS: m/z = 214, 216 $(M)^+$, 135 ($M^+ - CH_2Br$). Anal. calc'd for $C_8H_7BrO_2$: C 44.68, H 3.28; Found C 44.35, H 3.39. UV/Vis (DCM): 227, 268, 335 nm. IR: 3200, 1654, 1565, 1502, 1448, 1436, 1388, 1287, 1224, 1189, 1128, 1012, 974, 868, 802, 745, 664, 558, 453 cm^{-1}. M.P.: 50 °C (dec.).

Synthesis of monomer 2

A solution of 0.144 g (0.66 mmol) of **6** and 0.122 g (0.33 mmol) of **7** in 20 mL of degassed THF was stirred under N_2 at room temperature overnight. Nickel(II) acetate tetrahydrate (0.08 g, 4.5 mmol) was added and the red solution was stirred for an additional 12 h at room temperature. The solution was poured into 150 mL methanol, yielding a red precipitate. The precipitate was collected by filtration and reprecipitated 2 more times for purification. Yield: 0.15 g (0.18 mmol, 56%). ^1H NMR(trace of THF-d_8 in $CDCl_3$): $\delta = 7.78$ (s, 2H), 7.12 (d, 2H), 7.02 (s, 2H), 6.97 (s, 2H), 6.65 (d, 2H), 4.35 (s, 4H), 3.95 (d, 4H) 1.8–0.9 (m, 30H) ppm. ^{13}C NMR ($CDCl_3$): $\delta = 165.2$, 151.6, 150.4, 144.0, 136.3, 134.1, 121.9, 120.3, 116.6, 98.4, 77.4, 72.1, 39.9, 33.9, 30.8, 29.4, 24.2, 23.3, 14.3, 11.5 ppm. ESI-MS: $m/z = 814$ (M^+). Anal. Calc'd for $C_{38}H_{48}Br_2N_2NiO_4$: C 55.98, H 5.93, N 3.44; Found C 55.58, H 6.27, N 3.84. UV/Vis (THF): 263, 301, 391, 487 nm. IR: 3051, 3017, 2955, 2921, 2856, 1607, 1584, 1518, 1440, 1370, 1276, 1188, 1117, 1030, 944, 867, 824, 787, 744, 669, 617, 542, 458 cm^{-1}. M.P.: 160–162 °C.

Synthesis of polymer 8

To a stirred solution of 0.2 g (0.25 mmol) of monomer **2** in 10 mL of anhydrous THF and 10 mL of anhydrous DMF was added a solution of 0.05 g (4.5 mmol) of ^{t}BuOK in 5 mL THF. The resulting mixture was stirred for 48 h at room temperature before it was poured into methanol (150 mL). The red solid was collected by filtration and washed with methanol, then stirred in hexane at room temperature for 1 h. After drying in the funnel, the crude product was placed in a Soxhlet extractor and extracted into hot THF over 2 d. After cooling, the THF was removed by rotary evaporation to give a dark red solid (0.055 g, 34%). ^1H NMR (trace of THF-d_8 in CD_2Cl_2) δ = 9.0–8.2 (br), 8.0–6.4 (br), 4.0–3.6 (br) 1.8–0.9 (br) ppm. It was not possible to obtain a ^{13}C NMR spectrum. UV/Vis (THF): 225, 394 nm. IR: 3052, 3014, 2952, 2921, 2853, 1694, 1602, 1501, 1463, 1361, 1275, 1177, 1007, 866, 790, 723, 609, 530, 455 cm^{-1}. Theor. Anal. calc'd for HBr-terminated oligomers $BrH(C_{38}H_{46}N_2NiO_4)_4HBr$: C 65.77, H 6.75, N 4.04; Found: C 64.27, H 7.24, N, 4.18. GPC in THF showed oligomers, including a fraction with a molecular weight of M_n = 5560 Da.

Synthesis of complex 9

A mixture of 0.33 g (0.4 mmol) of **2** and 0.21 g (0.8 mmol) of PPh_3 in 40 mL of anhydrous DMF was heated to reflux for 8 h under nitrogen. After cooling to room temperature, the reaction mixture was poured into diethyl ether. The precipitate was collected on a Buchner funnel, washed with 100 mL of diethyl ether, and dried under vacuum. Yield: 0.26 g (0.24 mmol, 56%) of red solid. ^1H NMR (DMSO-d_6): δ = 8.92 (s, 2H), 7.3–7.9 (m, 48H), 6.65 (s, 2H), 6.10 (d, 2H), 5.09 (d, 4H), 3.95 (t, 4H), 0.8–1.8 (m, 30H) ppm. ^{13}C NMR (DMSO-d_6): δ = 163.9, 153.8, 150.6, 136.1, 135.2, 134.5, 130.5, 123.0, 121.2, 118.5, 117.7, 99.77, 77.4, 39.9, 31.3, 29.4, 23.9, 23.3, 14.3, 11.6 ppm. ^{31}P NMR (DMSO-d_6): $\delta = 23.45$ ppm. HRMS (ESI): $C_{74}H_{77}N_2NiO_4P_2$ Calc. 1177.4790, Found 1177.4712. UV/Vis (THF): 259, 389 nm. IR: 3053, 3013, 2953, 2925, 2858, 1602, 1512, 1435, 1374, 1278, 1191, 1109, 995, 870, 806, 743, 716, 687, 646, 606, 531, 503, 461 cm^{-1}. M.P.: 260 °C (dec.).

Synthesis of model compound 10

To a mixture of 0.1 g (0.07 mmol) of compound **9** and 0.015 g (0.14 mmol) of benzaldehyde was added 10 mL of dry THF and 10 mL of dry DMF. The mixture was stirred at R.T. for 10 min until all of the solid was dissolved. The solution was added under nitrogen by syringe to a flask containing 5 mL of dry THF containing 0.05 g (0.45 mmol) of ^{t}BuOK. After stirring for 8 h, the reaction mixture was poured into methanol. The precipitate was recovered by filtration and washed with 10 mL methanol. Yield: 0.042 g (0.05 mmol, 72%). ^1H NMR (CD_2Cl_2): $\delta = 8.02$ (br, 2H), 6.90–7.60 (br, m, 22H), 3.95 (br, 4H), 0.8–1.5 (br, 30H) ppm. ^{13}C NMR ($CDCl_3$): $\delta = 165.8$, 151.6, 150.0, 143.6, 137.3, 136.3, 133.3, 132.5, 131.6, 130.4, 129.36, 128.8, 128.3, 127.5, 127.1, 122.2, 120.4, 119.9, 116.9, 114.2, 98.5, 77.4, 72.2, 39.8, 30.8, 29.4, 24.1, 23.3, 14.3, 11.5 ppm.[32] HRMS (ESI): $C_{52}H_{58}N_2NiO_4$ Calc. 833.3750, Found 833.3828. Anal calc'd for $\mathbf{10} \cdot 2H_2O$ ($C_{52}H_{62}N_2NiO_6$): C 71.81, H 7.19, N 3.22; Found: C 71.67, H 6.81, N 3.43. UV/Vis (THF): 301, 406, 495 nm. IR: 3055, 3023, 2953, 2923, 2856, 1601, 1581, 1515, 1463, 1434, 1361, 1276, 1181, 1112, 1026, 958, 875, 778, 689, 634, 593, 529, 454 cm^{-1}. M.P.: 125–130 °C.

Conclusions

We have applied the Gilch polymerization method to construct a conjugated metal-containing analogue of poly(phenylenevinylene) (PPV). We synthesized a new monomer and demonstrated that polymerization affords gels or soluble oligomers. From GPC, the longest oligomers were *ca.* 7–8 repeat units in length. A model compound that represents a piece of the polymer was synthesized using a Wittig reaction. Our results show that the Gilch polymerization method may be applied to complex, metal-containing monomers to form novel soluble metallopolymers.

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