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Soluble and processable conjugated polyazines with oligo(*p*-phenylene vinylene)s

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Abstract

An efficient polycondensation reaction between α,ω-diformyl functional aromatics, namely 2,5-diheptyloxy-1,4-diformylbenzene and side-chain substituted α,ω-diformyl oligo(*p*-phenylene vinylene) (OPV) with hydrazine afforded novel soluble and processable conjugated polymers, **P1** and **P2**, respectively. The reaction conditions were investigated and structural analysis of the polymers was carried out by means of ^{1}H, ^{13}C, ^{15}N NMR, indicating all-*trans* configured C=N–N=C linkages. The molecular weights M_n were observed at ~1100–1400 g/mol for **P1** and ~8700–10,500 g/mol for **P2**. The optical properties showed absorption maxima at ~455 nm and ~487 nm for **P1** and **P2** ($CHCl_3$ solutions), respectively, red shifted by 31–60 nm relative to the monomer aromatics due to conjugation through the azine linkage. The emission maxima are observed at ~515 nm and ~560 nm for **P1** and **P2** ($CHCl_3$ solutions), respectively. Thin films of **P2** readily undergo n-doping.

Oligo(*p*-phenylene vinylene)s (OPVs) and their substituted derivatives belong to the family of conjugated materials with valuable opto-electronic properties such as photo/electroluminescence, photoconductivity, non-linear optical response and electrical conductivity after doping.[1–4] OPVs are well defined compared to higher molecular weight poly(*p*-phenylene vinylene)s. They are soluble and processable, making them attractive electronic building blocks for organic functionalization. Polyazines[5] (PAZs) are a type of poly Schiff-base polymers, and feature HC=N–N=CH linkages that are isoelectronic with butadienyl units, and thus seem suitable for conjugated organic materials. Typical characteristics of PAZs include thermal stability, strength, high modulus.[6] Some Schiff-base polymers have been receiving attentions due to their semi-conducting and non-linear optical properties recently.[7–10] Introducing flexible side chains to rigid polymers helps overcome the usually limited processability owing to high melting points and low solubility, thus enabling systematic structure/property investigations.[11] Soluble PAZs with alternating aromatic and azine units have been reported with substituted thiophene as the aromatic part.[12]

This Letter reports on the efficient polycondensation of dialdehyde functional OPV building blocks with hydrazine via azine formation, under mild conditions, affording soluble and processable materials. The products are rigid-rod type polymers featuring extended π-conjugated electron systems with integrated azine units and symmetrical side chain substitution at the OPV building blocks. The electronic character of the aromatic block can be tuned easily (i.e., size and type of aromat, different side chains). Specifically, this Letter presents the optimization of the coupling reactions of hydrazine with 2,5-diheptyloxy-1,4-diformylbenzene **1** and a homologous α,ω-aldehyde-functional trimeric diheptyloxy-OPV **2** (IUPAC: 2,5-Bis(heptyloxy)-1,4-bis-[2,5-bis(heptyloxy)-4-formyl-phenylene vinylene]benzene). **1** and **2** were synthesized in analogy to literature.[13] The polymer products **P1** and **P2** were analyzed in regard to size, microstructure, optical and electrochemical properties.

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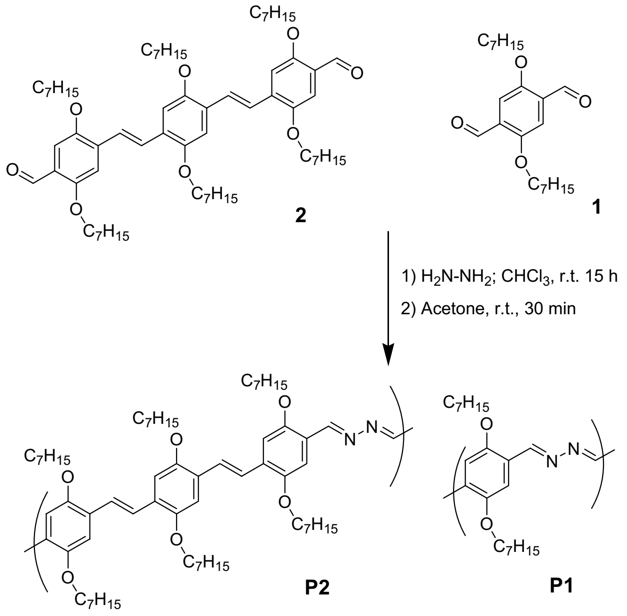

Scheme 1. Synthesis of polyazines **P1** and **P2**.

Scheme 1 summarizes the general approach and representative synthetic conditions. Typically, **1** or **2** was combined with equimolar amounts of hydrazine (hydrazine as a 1.0 M solution in THF).

The polymerizations were carried out in various solvents, that is, chloroform, THF, benzene, toluene, and dichloromethane, at ambient (25 °C) or slightly elevated temperatures (up to 50 °C) in the case of **P2**, as illustrated in Table 1.[15,16] Usually precipitate appears 2–3 h after the reaction starts. After an appropriate reaction time, acetone was added to 'deactivate' unreacted hydrazine and 'cap' any amine chain ends. Volatiles were then removed under vacuum.

In the case of **P1**, ~10–15% by weight insoluble residues were obtained when using $CHCl_3$ or $CDCl_3$ as the main reaction solvent (Table 1, # 1–3). Molecular weight analysis was carried out via size exclusion chromatography (SEC) in THF, thus all presented molecular weights are representative only of the THF soluble fraction of the products (lower product solubility in THF). Reactions in benzene, toluene, THF, or dichloromethane as (Table 1, # 4–7) resulted in less soluble products **P1**, rendering SEC no longer meaningful. This observed behavior is counter-intuitive in the case of the reaction in THF (Table 1, # 7), where the overall molecular weights were expected to be lower. Further investigations to explain this observation are under way. In the case of the isolated product mixtures of **P2** (Table 1, # 8–10), the insoluble residues were less, ~5–10% by weight. Also, the solubility of **P2** in THF was significantly higher than in the case of **P1**, making the presented molecular weights and distributions more representative. The increased solubility can be attributed to more flexible side chains per repeat unit.

Figure 1 summarizes representative SEC- traces of the THF-soluble fractions of **P1** and **P2**, together with SEC- traces of monomers **1** and **2** (**P1** traces normalized to the signal from the dimer fraction at ~36.5 min). The molecular weights M_n of the THF-soluble fractions of **P1** and **P2** typically are in the range of ~1100–1400 g/mol and ~8700–10,500 g/mol, respectively, relative to polystyrene standards. Longer reaction times lead to increased M_n's. Also, reactions in $CHCl_3$ resulted in higher molecular weights compared to CH_2Cl_2 (Table 1, # 8 vs # 9). Even after 10 min of reaction time SEC traces of **P1** indicate significant product formation. This is supported by corresponding time-dependent ^1H NMR spectra (not shown).

^1H NMR spectra of the **P1** reaction mixtures exhibit characteristic resonances for the azine at ~9.05 ppm and aromatic protons at ~7.7 ppm almost immediately upon combination of the monomers. ^{15}N NMR spectra (gHMBC) confirm the presence of only one nitrogen

Table 1
Representative syntheses of **P1** and **P2**

Polymer	#	Conditions[a] Solvent/t (h)/T (°C)	Yield[b] (%)	M_n[c], M_n/M_w
P1	1	$CHCl_3$/5/25	92	1418, 1.3
	2	$CHCl_3$/3/25[d]	96	1135, 1.2
	3	$CDCl_3$/3/25[e]	92	1251, 1.3
	4–7	Benzene, toluene, CH_2Cl_2, THF/12/25	93–94	n.a.
P2	8	CH_2Cl_2/THF (1/1 v/v) /16/25	92	8701, 2.4
	9	$CHCl_3$/16/25	90	10468, 1.8
	10	THF/24/50	95	10324, 2.3

[a] [**1**, **2**]/[hydrazine] = 0.10 M/0.10 M, 1.0 M hydrazine in THF.
[b] Isolated mass.
[c] THF-soluble fraction, relative to polystyrene standards; n.a. not applicable (insoluble in THF).
[d] [**1**]/[hydrazine] = 0.15 M/0.10 M.
[e] [**1**]/[hydrazine] = 0.030 M/0.030 M.

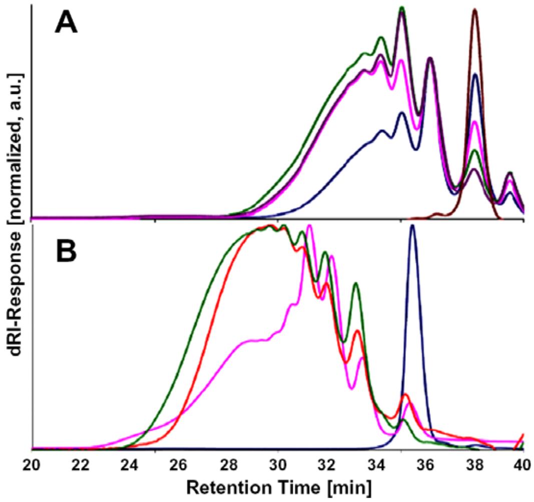

Fig. 1. SEC-Traces; A: **1** (—) and **P1** (Table 1, # 3) at different reaction times: 10 min (—), 30 min (—), 80 min (—), 170 min (—); B: 2 (—) and **P2** (Table 1): entry #'s 8 (—), 9 (—), 10 (—).

species with a single resonance at ~376 ppm, corresponding to the *s*-trans conformer with respect to the C=N–N=C linkage, and yielding an efficiently delocalized electron system. We always observe residual signal intensity from aldehyde-protons in the spectra of **P1** and **P2**. These signals at ~10.5 ppm are due to unreacted monomers **1** and **2** in the condensation mixtures (also observed in the SEC traces of **P1** and **P2** at ~38 min and ~35.5 min, respectively). No chain-end specific aldehyde-protons could be assigned via NMR. Efforts to elucidate the chain end functionality are ongoing. In the case of **P2**, the azine proton resonance is observed at ~9.15 ppm, also corresponding to the *s*-trans conformation. This is corroborated by ^{15}N NMR with one single resonance at ~373 ppm. Integration of the NMR-signals confirms the presence of two azine protons per repeat unit in **P1** and **P2**.

ATR/FTIR spectra of **1**, **2**, **P1**, and **P2** (Fig. 2, top) indicate the strongly reduced C=O stretching band at 1678 cm^{-1} and the appearance of C=N stretching at 1604 cm^{-1} in **P1** and at 1612 cm^{-1} in **P2** (visible as a shoulder on the C=C stretching at 1595 cm^{-1}). Also, in **P1** there is a noticeable change of the aromatic out-of-plane deformation (875 cm^{-1}), relative to 1 (893 cm^{-1}), and of the aromatic C–H deformations at 1194 and 1036/1017 cm^{-1} versus 1214 and 1039/1006 cm^{-1}, respectively. These changes are less pronounced in **P2** due to the larger aromatic segment. The strong C=O vibration is always visible in both products, in accordance with the less sensitive NMR spectra.

The optical properties of **P1** and **P2** were investigated in chloroform (Fig. 3) and THF. Absorptions in $CHCl_3$ show the expected red shifted maxima in **P1** and **P2** (455 and 487 nm, respectively) relative to the starting compounds **1** and **2** (404 and 447 nm, respectively). This is due to the extended conjugation through trans-configured azine double bonds and the aromatic building blocks. The overall shift from **1** to **P1** is larger than the shift from **2** to **P2** (−0.344 vs −0.231 eV), respectively, because the chain extension by adding a repeat unit to **1** is a larger change relative to the existing conjugated system. No significant differences between the absorption behaviors of THF soluble and $CHCl_3$ soluble fractions (higher M_n) or between individual product batches were observed. Apparently, the maximum effective conjugation length has been achieved,[14] yet the products remain soluble and processable. Corresponding solutions of **P1** and **P2** in THF (not shown) exhibit slightly blue-shifted absorption maxima at ~452 and ~482 nm. The observed emission behavior was analogous to the absorption, with maximum emission wavelengths for **1, P1** and **2**, **P2** at ~465, ~515 nm, and ~518, ~560 nm, respectively (**1**, **2** in Supplementary data). The emission spectrum of **P1** shows shoulders at ~544 and ~646 nm. Similar long wavelength components are observed in the emission spectrum of **P2** (smaller shoulders at ~610 and ~650 nm).

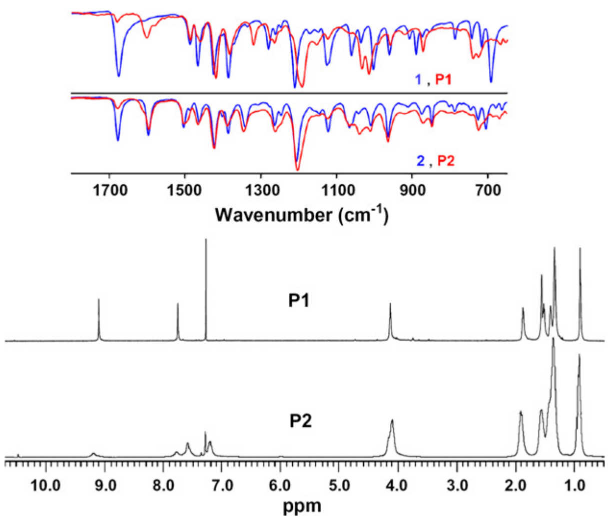

Fig. 2. ^{1}H NMR (bottom, 600 MHz; $CDCl_3$); **P1**, **P2**; ATR/FTIR spectra; (top): **1**/**P1**, **2**/**P2**.

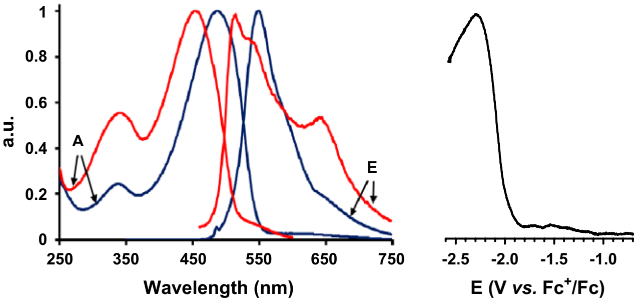

Fig. 3. Left: UV/vis absorption (**A**, ~10^{-4} M and fluorescence spectra (**E**, ~10^{-6} M), normalized in $CHCl_3$) **P1** (—), **P2** (—); right: differential pulsed voltammogram of **P2** film on Pt electrodes in acetonitrile solution.

To our surprise, thin films of **P2** show a strong metallic luster. However, electrical conductivity measurements indicate that they are insulators, which is supported by the absence of any broad near-IR bands. Differential pulsed voltammetry (DPV) of **P2** film on a Pt electrode was performed to investigate the electrochemical characteristics. A representative DPV reduction scan is shown as the right graph in Figure 3. The reduction (n-doping) occurred at −2.29 V, versus the Fc^{+}/Fc couple. Repeating the reduction cycle between 0 and −2.5 V leads to gradual degradation of the sample. An oxidation scan (tested from 0 to 2 V) results in irreversible oxidation (at 0.88 V and 1.44 V versus the Fc^{+}/Fc couple), indicating that the polymer **P2** has more n-type characteristics, whereas conjugated polymers of the PPV type usually display *p*-type behaviors.

In summary, we have presented an effective way to synthesize soluble and processable conjugated polymers containing easily customizable aromatic OPV units alternating with azine linkages, thus integrating nitrogen into the conjugated chain. The chains are *trans* configured at the azine bonds, and the azine represents the homologue of a butadienyl bridge in the conjugated chain. **P2** readily undergoes n-doping.

Acknowledgments

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Supplementary data

Synthetic procedures with additional characterization of **P1**, **P2** (^{1}H NMR spectra, ^{15}N NMR, FT/IR, UV/vis absorption, and emission spectra, including **1** and **2**). Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2007.12.002.

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15. Typical synthesis of **P1**: 2,5-Bis(heptyloxy)terephthaldehyde 1 (0.5 mmol) in 5 mL of appropriate dry solvent was stirred at room temperature, and then hydrazine (0.5 mmol, 1 M solution in THF) was added slowly under argon. The reaction mixture was stirred at room temperature for given time, or until only traces of aldehyde peak could be observed in the ^{1}H NMR. To the reaction mixture a small amount of acetone (1 mL) was added, and stirring was continued for an additional 30–60 min. Finally, all volatiles/solvents were evaporated under vacuum to isolate a deep yellow-orange solid (**P1**). Isolated yield: 96%; ^{1}H NMR (600 MHz, CDCl$_3$): $\delta = 9.06$ (s, C=NH, 2H), 7.72 (s, ArH, 2H), 4.11 (m, –OCH$_2$, 4H), 1.85–1.1 (m, –CH$_2$–,10H), 0.89 (t, –CH$_3$, 6H) ^{15}N NMR (60 MHz, CDCl$_3$): $\delta = 376$ (C=N–N=C); FTIR (ATR, cm^{-1}): 3012, 2927, 2880, 1604, 1584, 1489, 1463, 1126, 875, 791, 777. More details in Supplementary data.
16. Typical synthesis of **P2**: 2,5-Bis(heptyloxy)-1,4-bis[2,5-bis(heptyloxy)-4-formyl-phenylene vinylene]benzene **2** (0.5 mmol) in 5 mL of appropriate dry solvent was stirred at room temperature, and then hydrazine (0.5 mmol, 1 M solution in THF) was added slowly under argon. The reaction was stirred at slightly elevated temperature (50 °C) for a given period of time, and/or monitored by means of ^{1}H NMR. To the reaction mixture a small amount of acetone (1 mL) was added, and stirring was continued for an additional 30–60 min. Finally, the reaction mixture was cooled to room temperature and all volatiles/solvents were evaporated under vacuum to isolate a deep orange-red color solid with a strong metallic cluster (**P2**). Isolated yield: 92%; ^{1}H NMR (600 MHz, CDCl$_3$): $\delta = 10.431$ (s, terminal CHO, 2H), 9.14 (br, C=NH, 2H), 7.72 (br, ArH, 2H), 7.54 (br, –CH=CH–, 2H), 7.31 (s ArH, 2H), 7.16 (br, ArH, 2H), 4.07 (m, –OCH$_2$, 12H), 1.87–1.1 (m, –CH$_2$–, 60H), 0.87 (t, –CH$_3$, 18H). ^{15}N NMR (60 MHz, CDCl$_3$): $\delta = 372.7$ (C=N–N=C); FTIR (ATR, cm^{-1}): 3058, 2921, 2871, 1612, 1597, 1465, 1066, 848, 726. More details in Supplementary data.