Conjugated Polymers

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Soluble Poly(*p*-phenylenevinylene)s through Ring-Opening Metathesis Polymerization**

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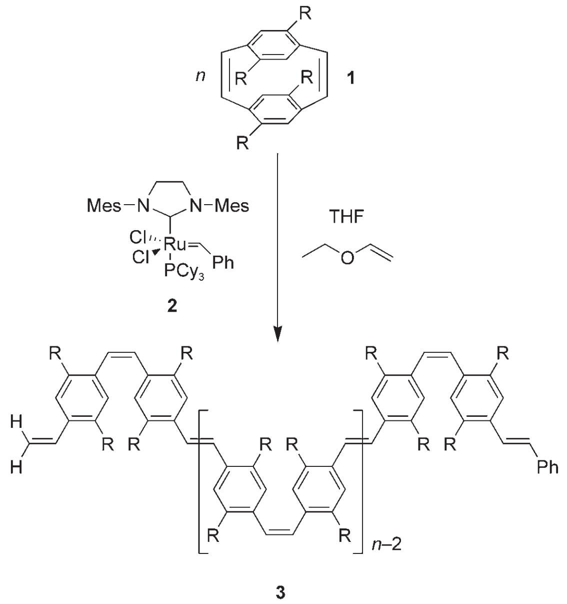
Soluble semiconducting polymers are attractive synthetic targets as they can be deposited from solution using low-cost processing routes to fabricate organic electronic devices such as light-emitting diodes, photovoltaics, and field-effect transistors.[1] One of the most widely studied systems are the poly(*p*-phenylenevinylene)s (PPVs), first reported by Burroughes et al. to show electroluminescence in polymeric light-emitting diodes.[2] The parent unsubstituted PPV is insoluble, and substituents are appended to the phenylene groups to produce soluble PPVs. A number of synthetic routes to these polymers has been described,[3] but all of these routes lead to polydispersities consistent with termination processes and consequently these are not living polymerizations.

Ring-opening metathesis polymerization (ROMP) offers the opportunity for precise control of the conjugated-polymer molecular weight, low polydispersities, and the preparation of block copolymers. This method has been applied to the synthesis of polyacetylene by Feast et al.[4] and has been exploited in the synthesis of PPV polymers and copolymers.[5,6] Initial reports focused on the preparation of precursors that can be converted into insoluble PPV homopolymer. ROMP of [2.2]paracyclophane-1,9-diene gives PPV directly as an insoluble yellow fluorescent powder. Soluble copolymers of PPV have been prepared by ROMP with cyclopentene, cyclooctene, and cyclocta-1,5-diene comonomers. However, incorporation of more than 5 % of PPV units gives insoluble polymers.[6] Herein we report the first polymerization of substituted [2.2]paracyclophanedienes using ruthenium-based metathesis catalysts to give monodisperse, soluble phenylenevinylene homopolymers.

The ROMP of the tetra-alkoxy-substituted [2.2]paracyclophanediene derivative **1**, dissolved in THF, was initiated by addition of a THF solution of the second-generation Grubbs catalyst **2** (Scheme 1).[7] The reaction mixture was heated at reflux and then quenched by addition of ethyl vinyl ether. The resulting polymers **3** were purified by filtering through silica gel and isolated by evaporation of the solvent. Polymers with a range of molecular weights were prepared by varying the monomer-to-catalyst ratio. An extended reaction time (36 h) was necessary to achieve complete conversion of monomer, indicating a slow rate of polymerization.[5b,8]



Scheme 1. ROMP of cyclophanediene **1** to give monodisperse, soluble PPVs **3**. $R = OC_8H_{17}$.

The molecular weights of the polymers were determined by gel permeation chromatography (GPC) in THF solution. The number-average molecular weight (M_n) increased monotonically with the initial monomer-to-catalyst ratio (Figure 1) with a correlation coefficient of 0.999, and the polydispersities were all close to 1.2. The apparent discrepancy between the expected and the observed molecular weights (Figure 1) is due to the difference in the hydrodynamic radii of PPV and polystyrene.[9] From the linear relationship between the monomer-to-catalyst ratio and the degree of polymerization, the low polydispersities, and the complete consumption of monomer, we conclude that chain transfer, back-biting, or termination are absent and the polymerizations could be regarded as living.[10,11]

The living nature of this polymerization was confirmed by an experiment in which a second charge of monomer was added to the polymerization reaction. The initial reaction gave a polymer with $M_n = 7428$ (expected $M_n = 7264$) and a polydispersity of 1.20. A second addition of one third amount of monomer increased M_n to 9554 (expected $M_n = 9412$;

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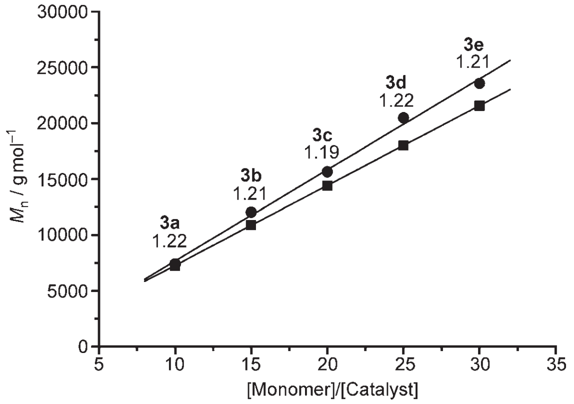

Figure 1. Dependence of the molecular weight (M_n) of polymer **3** on the ratio **1**/**2**. The polydispersities are given for expected $n = 10$, 15, 20, 25, 30. ●: GPC with refractive index (RI) detection; ■: calculated.

polymer **3 f**) with no change in the polydispersity (Figure 2), consistent with a living polymerization and demonstrating the potential of this chemistry to prepare conjugated block copolymers.

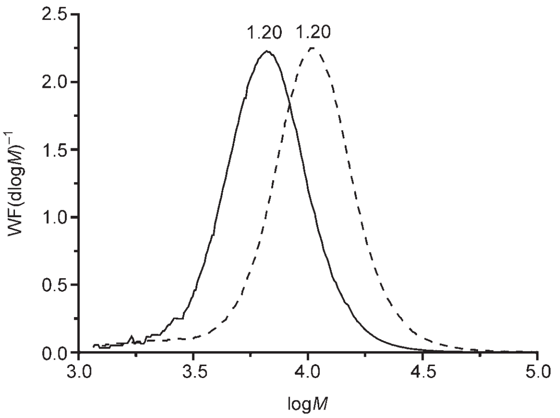

Figure 2. Molecular weight (M) distribution and polymer dispersities for stepwise synthesis of a polymer from $n = 10$ (solid line) to $n = 13$ (dashed line), using calculated Mark–Houwink parameters.

The MALDI-TOF mass spectrum of polymer **3a**, isolated by a single filtration through silica gel followed by washing with methanol, shows a series of peaks separated by an interval of 716 mass units, corresponding to the molecular weight of the monomer (Figure 3). This series is consistent with PPVs capped with vinyl and phenyl end groups, as expected, and is accompanied by peaks associated with the addition of one sodium ion per polymer chain. There was no evidence for the defect structures commonly seen for other synthetic routes.[3]

The ^{1}H NMR spectrum of **3** showed the high level of control achieved in this polymerization (Figure 4). Relief of significant ring strain within monomer **1** is achieved by opening of only one vinylene linkage and it is expected that polymer **3** has a backbone of regularly alternating *cis* and *trans* vinylene linkages. Peaks at $\delta = 3.96$ and 3.50 ppm can be assigned to the methylene groups attached to oxygen atoms for the *trans* and *cis* vinylene links of the polymer backbone, respectively.[12,13] Integration of these signals gave the expected 1:1 ratio. The precise control of the polymer microstructure was confirmed by the simplicity of the NMR signals associated with the aromatic and vinylene groups (i.e., the peaks between $\delta = 6.60$ and 7.50 ppm). The signals at $\delta = 6.66$ and 6.83 ppm are associated with the aromatic and *cis* vinylene units, respectively; whereas those at $\delta = 7.35$ and 7.10 ppm are assigned to hydrogen atoms of the *trans* vinylene and associated aromatic groups. Again the integration of these signals is consistent with a 1:1 ratio of *cis*/*trans* linkages.

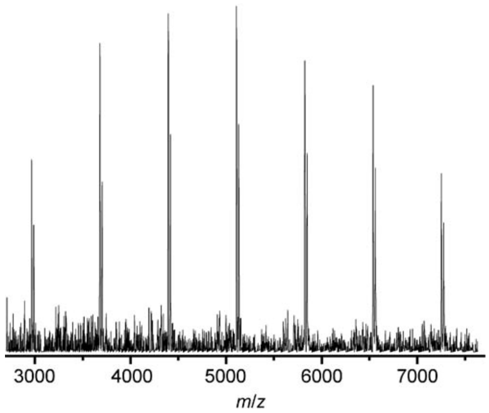

Figure 3. MALDI-TOF mass spectrum of polymer **3a** (expected: $n = 10$).

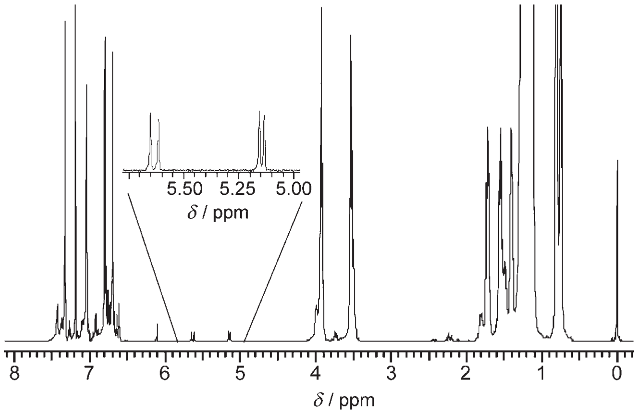

Figure 4. ^{1}H NMR spectrum of **3 f** in $CDCl_3$ solution. The inset shows an expansion of the signals associated with the vinyl end groups.

Further evidence for the structure of **3** was the presence of C–H out-of-plane deformation vibrations for the *cis* and *trans* vinylene links, at 850 and 965 cm^{-1}, respectively, in the FTIR spectra (see Supporting Information). Absolute values for the degree of polymerization were determined by integration of the signals for the vinyl end groups observed at $\delta = 5.15$ and 5.64 ppm against those for the methylene groups attached to oxygen atoms. In all cases the values obtained are consistent with the expected number of repeat units, derived from the monomer-to-catalyst ratio (Table 1).

It has been previously reported that the physical properties of PPVs are strongly dependent on the configuration of the vinylene units.[14–16] Son et al. demonstrated that PPVs

Table 1: Molecular weight, UV/Vis, and photoluminescence (PL) data for **3 a–f**.

3, *n*	M_n[a]	M_n[b]	PDI[b]	M_n[c]	λ_{max}^{Abs} [nm][d]	λ_{max}^{PL} [nm][d]
3 a, 10	7264	7428	1.22	7207	482	556
3 b, 15	10844	12025	1.21	10570	491	556
3 c, 20	14424	15644	1.19	15235	496	557
3 d, 25	18004	20492	1.22	17745	497	556
3 e, 30	21584	23584	1.21	[e]	502	557
3 f, 13	9412	9554	1.20	9548	490	556

[a] Expected M_n (including end groups). [b] Determined by GPC with RI detection. [c] Determined by ^{1}H NMR spectroscopy. [d] In CH_2Cl_2. [e] Intensity of the signals for vinyl end groups comparable to spectral noise.

having a moderate ratio of *cis* and *trans* vinylene units exhibited higher electroluminescence efficiencies than the all-*trans* analogues.[12,14,15] UV/Vis spectroscopy (Figure 5) shows that the wavelength of the absorption maximum for **3** increases with the polymer chain length and hence the conjugation length increases. The photoluminescence spectra recorded for **3** (Figure 5) are identical as emission occurs from the most conjugated segment of the polymer, regardless of the chain length.

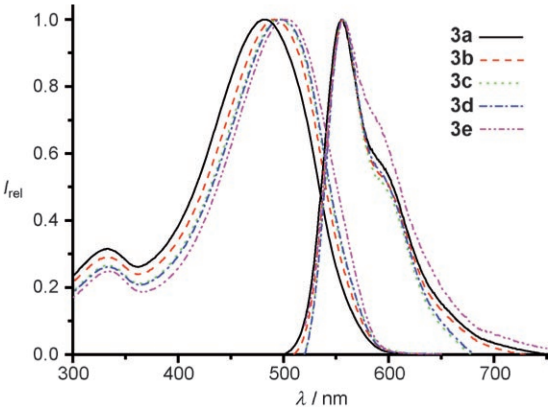

Figure 5. UV (left) and PL (right) spectra of **3 a–e**.

In summary, soluble PPV homopolymers of well-defined molecular weight with an alternating *cis-trans* microstructure can be prepared by ROMP. The living character of this polymerization has been demonstrated by controlled chain extension on addition of additional monomer. This approach has tremendous potential in the preparation of well-defined PPV block copolymers, and the synthesis of these materials is the focus of ongoing investigation.

Experimental Section

All experiments were performed under a nitrogen atmosphere in a Radleys GreenHouse or by using standard Schlenk techniques. All reagents were used as received from commercial suppliers without further purification. THF was distilled over sodium/benzophenone ketyl under dry nitrogen. Monomer **1** was prepared by a modification of established procedures.[17]

Synthesis of **3a–f**: In a nitrogen-filled Radleys GreenHouse, monomer **1** (50.1 mg, 0.07 mmol) was charged into five separate tubes and dissolved in 1.2, 0.8, 0.6, 0.48, and 0.4 mL of dry THF. Catalyst **2** (23 mg) was dissolved in 2 mL of dry THF and stirred for at least 10 min to fully dissolve. Aliquots of the catalyst solution (517, 345, 258, 207, and 172 μL) were added into the monomer solutions, and the GreenHouse was heated at 68 °C for 36 h. The reaction mixtures were cooled to room temperature, and excess ethyl vinyl ether (2 mL) was added to quench the reaction. After stirring for a further 4 h at room temperature the reaction mixtures were concentrated under vacuum. The products were redissolved in chloroform and filtered through a short plug of silica to remove the catalyst. The solvent was removed under reduced pressure, and the resulting solid was exhaustively washed with methanol. The polymers obtained were dried under vacuum at 40 °C for 24 h. Yields ranged from 93 to 98 %.

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