Stereoretentive Ring-Opening Metathesis Polymerization to Access All-*cis* Poly(*p*-phenylene vinylene)s with Living Characteristics

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ABSTRACT: Poly(*p*-phenylene vinylene)s (PPVs), a staple of the conductive polymer family, consist of alternating alkene and phenyl groups in conjugation. The physical properties of this organic material are intimately linked to the *cis/trans* configuration of the alkene groups. While many synthetic methods afford PPVs with all-*trans* stereochemistry, very few deliver the all-*cis* congeners. We report herein the first synthesis of all-*cis* PPVs with living characteristics via stereoretentive ring-opening metathesis polymerization (ROMP). Exquisite catalyst control allows for the preparation of homopolymers or diblock copolymers with perfect stereoselectivity, narrow dispersities, and predictable molecular weights. All-*cis* PPVs can then serve as light-responsive polymers through clean photoisomerization of the stilbenoid units.

Although new architectures are regularly reported, the poly(*p*-phenylene vinylene)s (PPV) family remains one of the most studied types of conjugated polymers (Figure 1).[1] PPV was used to make the first organic light-emitting diode (OLED),[2] and was one of the components blended into the first "bulk heterojunction" solar cells.[3] The relative stability of PPV and its desirable semi-conducting properties (i.e., band gap in the visible range) have motivated numerous academic and industrial research groups to explore its optoelectronic properties.[4] This effort led to many robust syntheses of PPVs, including controlled polymerizations, with high molecular weights (M_n).[5,6] One distinctive feature of PPVs is the presence of a stilbenoid olefin in the repeating unit. The *cis* or *trans* (*Z* or *E*) configuration of the olefins dramatically affects the overall properties of the material. *Cis*-rich PPVs are characterized by a twisted and coiled polymer chain, whereas *trans*-rich PPVs possess a rod-like structure which increases π–π interactions and packing. As a result, *cis* alkenes tend to decrease the effective conjugation length of the polymer but increase its solubility.[7,8] Additionally, one-way[9] photochemical isomerization rapidly transforms *cis* into *trans* linkages. This clean photoisomerization has been exploited by Katayama and coworkers to pattern PPVs, capitalizing on the difference in solubility between *cis* and *trans* congeners,[10] and by Choi to prepare semiconducting nanofibers via controlled self-assembly.[11,12] In an effort to harness the full potential of PPVs as stimuli-responsive material, we report herein the first synthesis of all-*cis* PPVs with living characteristics in homopolymers and block copolymers.
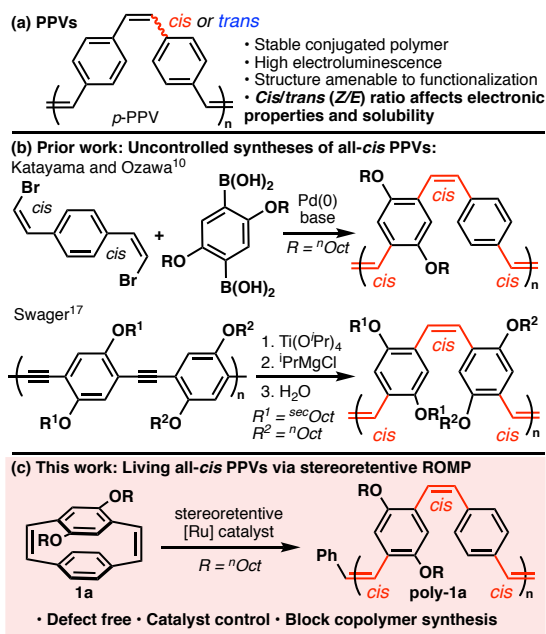

Figure 1. a) General structure of poly(*p*-phenylene vinylene)s (PPVs). b) The only two examples of uncontrolled synthesis of all-*cis* PPVs. c) A stereoretentive ROMP strategy en route to all-*cis* PPVs with living characteristics.

Syntheses of all-*cis* PPVs are far scarcer than that of all-*trans* PPVs. Indeed, Wittig,[13] Horner-Wadsworth-Emmons,[14] or Knoevenagel[15] polycondensations either lead to an uncontrolled *cis/trans* ratio, or favor *trans* olefins. Radical or anionic polymerization of *p*-quinodimethane during the Gilch process also favors the more stable *trans* linkage.[5,6] In 2005, Katayama and Ozawa reported a stereospecific Suzuki-Miyaura polymerization that affords low molecular weight all-*cis* PPVs with selectivities up to 99:1 using linear monomers with preinstalled *Z*-stereochemistry.[10,16] In a different approach, Swager and coworkers synthesized all-*cis* PPVs via post-polymerization reduction of poly(phenylene ethynylene)s (PPEs) with stoichiometric titanium isopropoxide and isopropyl magnesium chloride.[17] Both routes afforded impressive stereoselectivity, but are based on uncontrolled chain-growth polymerization, which limits their application to the synthesis of macromolecular constructs. Our strategy to access all-*cis* PPVs with living characteristics relied on the polymerization of paracyclophane diene monomers (Figure 1C, **1a**) via ring-opening metathesis polymerization (ROMP). Early studies from Turner demonstrated that these strained alkene monomers could undergo efficient ROMP, leading to PPVs with alternating *cis* and *trans* linkages using Grubbs 2nd generation catalyst (**2a**) (see Figure 2 for catalyst structures).[18–20] The *trans* alkenes are postulated to arise from isomerization driven by the catalyst during ROMP. We hypothesized that either *Z*-selective[21] or stereoretentive[22–24] metathesis catalysts could allow for the controlled preparation of all-*cis* PPVs with predictable high M_n's, low Đ's, and little to no *trans* defects. While *Z*-selective catalyst **2c** has been applied to polymerize a variety of norbornene derivatives,[25] stereoretentive dithiolate-chelated Ru catalysts such as **2d** have seldomly been used for ROMP. Only norbornene,[22,26] cyclooctadiene,[22] and norbornadiene[27] have been polymerized with this new generation of catalysts that enables retention of the alkene stereochemistry during metathesis.[28] Importantly, perfect *cis* control in the ROMP process was targeted since any post-polymerization isomerization would lead to all-*trans* PPVs.[29–31]
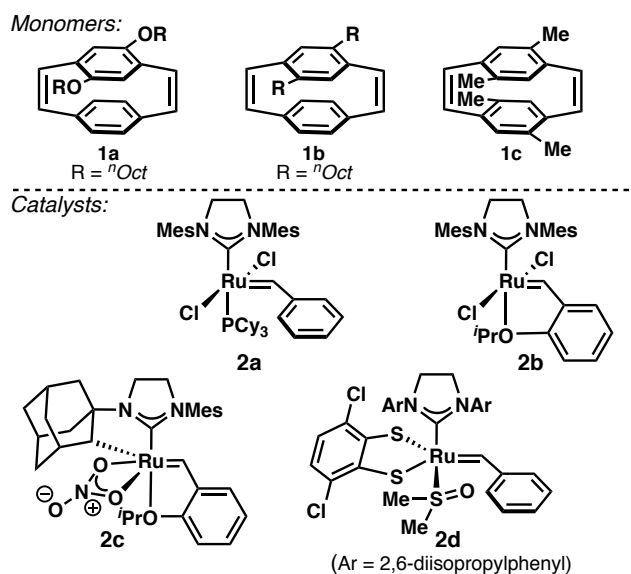

Figure 2. Paracyclophane diene monomers **1a–c** and olefin metathesis catalysts **2a–d** used for the initial screening. Mes = mesityl, Cy = cyclohexyl.

Olefin metathesis catalysts **2a–d** were selected for the initial screening, and paracyclophane diene monomers **1a–c** were synthesized using literature procedures (Figure 2).[19,32] While monomers **1a** and **1b** successfully polymerized with all catalysts, **1c** only afforded small polymers with **2a** and **2b**, and did not polymerize with **2c**, which was ascribed to increased steric hindrance around the alkenes when both rings are substituted. In contrast to **poly-1a**, determination of the stereoselectivity by 1H-NMR in **poly-1b** was complicated by the overlap of the key signals (see Supporting Information). The determination of catalyst stereocontrol was therefore achieved by examining the ratio of *cis* and *trans* linkages in polymers obtained with catalysts **2a–d** and monomer **1a** using 1H-NMR (Figure 3).[10] In THF at 60 °C, Grubbs 2nd generation (**2a**) afforded a *p*-PPV with a 59:41 ratio in favor of the *trans* alkenes. The deviation from the expected 1:1 ratio might be due to thermal isomerization under these conditions. Hoveyda-Grubbs 2nd generation (**2b**) delivered a similar result with a ratio that is even more skewed toward *trans* alkenes (65:35). As hypothesized, switching to the commercially available *Z*-selective catalyst **2c** inversed that ratio, with 66% of the olefins now being *cis*-configured. To our

delight, complete *cis* selectivity (> 99:1) was observed using stereoretentive catalyst **2d** recently synthesized by Materia Inc.[33] Following ROMP with **2d**, no *trans* linkages could be detected in poly-**1a** within the limits of sensitivity of ^{1}H-NMR.
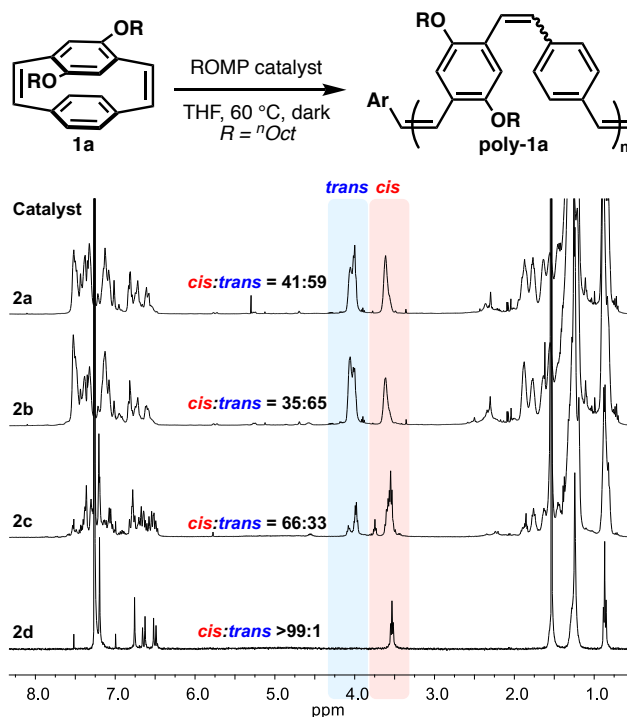

Figure 3. ^{1}H NMR comparison of *p*-PPV poly-**1a** synthesized with catalysts **2a–d** in THF at 60 °C in the dark for 24 h. At the chain-end, Ar = Ph for **2a,d** and 2-isopropoxyphenyl for **2b,c**.

The reaction conditions using **2d** were then optimized in order to furnish PPVs with living characteristics using **2d**. Polymerizations were kept in the dark to avoid photoisomerization, and conducted in the glovebox because **2d** proved to be sensitive to oxygen in solution. Maintaining a reaction temperature of 40 °C in THF not only delivered exquisite control of the configuration of all alkenes in the backbone, but also allowed for the preparation of PPVs with predictable M_n's up to 14.3 kg/mol and low *Đ*'s by varying the ratio of monomer **1a** to catalyst **2d** (Table 1). As expected for controlled polymerization, a linear relationship between M_n and monomer conversion was observed by monitoring the polymerization of **1a**, and dispersity values remained between 1.4 and 1.5 throughout the ROMP (Figure 4a). Notably, full conversion can be reached without loss of control over the molar mass distribution.

Table 1. ROMP of **1a** catalyzed by **2d**.

Entry[a]	1a:2d ratio	1a conversion	M_n theo (kg/mol)	M_n exp (kg/mol)	*Đ*
1	10:1	100%	4.6	5.4	1.43
2	20:1	100%	9.2	9.6	1.51
3	30:1	100%	13.8	14.3	1.52

[a]**1a** (0.05 mmol) was polymerized with **2d** at 40 °C in THF in the dark and under nitrogen for 4 h. M_n's and *Đ*'s were determined by SEC (THF) using polystyrene standards (RI detection).
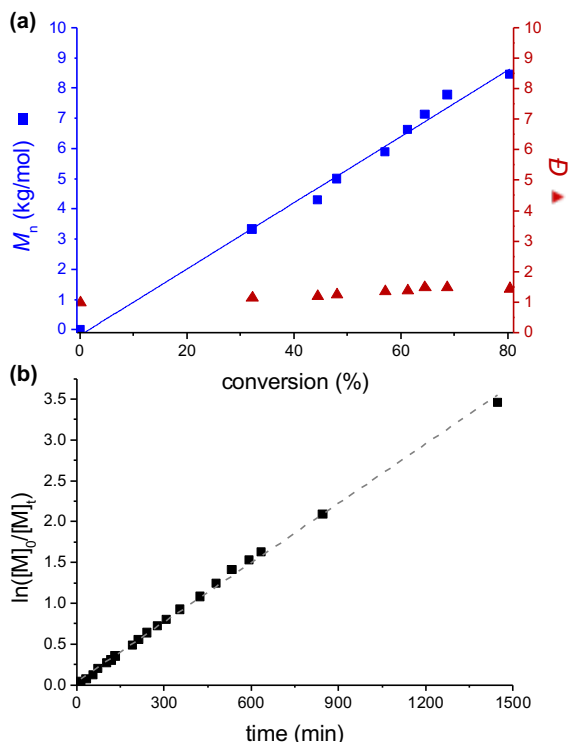
Figure 4. Polymerization of **1a** with catalyst **2d**: (a) M_n and $Đ$ vs conversion. (b) Determination of the rate of propagation ($R^2 = 0.99795$). Kinetic studies were performed at room temperature to slow down the propagation and to allow for the collection of data points over a convenient length of time.

The kinetics of ROMP with monomer **1a** and catalyst **2d** was compared to that of other Grubbs catalysts. Assuming a typical living polymerization process, the apparent propagation rate was calculated using equations (1) and (2):

$$-\frac{d[M]}{dt} = k_p^{\text{app}}[M_t] \qquad (1)$$

$$k_p^{\text{app}} = k_p[C_t] \qquad (2)$$

where $[M_t]$ is the concentration of monomer **1a** at time t, k_p^{app} the apparent propagation rate constant, k_p the propagation rate constant, and $[C_t]$ the concentration of **2d** at time t. Plotting $\ln([M_0]/[M_t])$ as a function of time revealed a linear fit and a k_p^{app} value of 0.00243 min^{-1}, which is of the same order of magnitude as with Grubbs 2nd generation (**2a**) with the same monomer, and one order of magnitude lower than with Grubbs 3rd generation according to mechanistic studies by Turner,[34] and Zentel and Choi.[35] Interestingly, the rate of initiation was too high to be calculated by NMR since all of catalyst **2d** had reacted with **1a** before the first spectrum could be collected. This extremely fast initiation at room temperature is undoubtedly key to the observed control over M_n and constitutes a notable difference with the Grubbs catalysts previously used with **1a**.
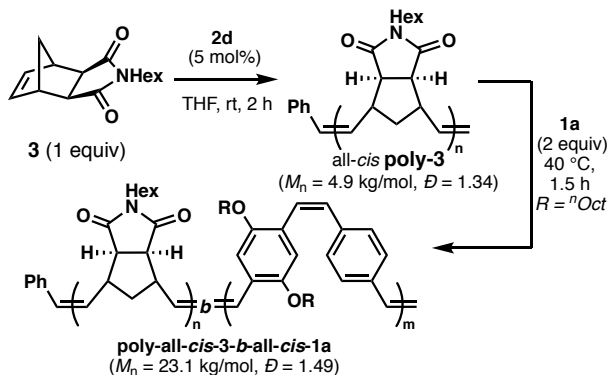

Figure 5. Synthesis of all-*cis* **poly-3** and **poly-all-*cis*-3-*b*-all-*cis*-1a** via chain extension.
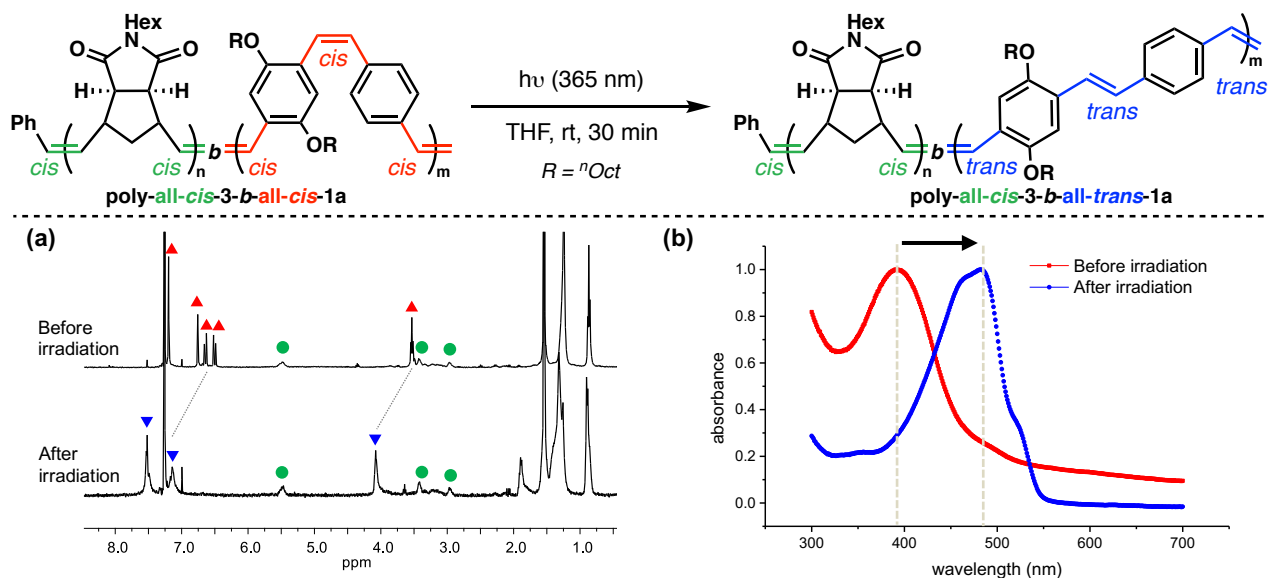
Figure 6. Photoisomerization **poly-all-*cis*-3-*b*-all-*cis*-1a**: a) 1H-NMR spectra. Characteristic peaks are indicated as follows: all-*cis* **poly-1a** block (red triangles), all-*trans* **poly-1a** block (blue triangles), all-*cis* **poly-3** block (green circles). b) UV-visible absorption spectroscopy before and after UV light (365 nm) irradiation.

By contrast to the prior syntheses of all-*cis* PPVs,[10,17] the living behavior of the ROMP process enables functionalization of the chain-end of all-*cis* **poly-1a**, as well as chain-extension to access multiblock copolymers. In order to investigate the responsiveness of all-*cis* PPV **poly-1a** to light within intricate polymeric architecture, block copolymers containing a block of **1a** and a block of *exo*-norbornene-imide **3**[36,37] were prepared. The excellent chain-end fidelity observed with the stereoretentive ROMP allowed for the synthesis to start with either block (Figure S12–S16). However, chain extension of **poly-3** with **1a** helped increase the size of the PPV segment despite its intrinsically low solubility (Figure 5). In line with the stereoretentive ROMP of norbornene reported by Hoveyda,[22] only *cis* linkages were identified in **poly-3** by NMR. With **poly-all-*cis*-3-*b*-all-*cis*-1a** in hand, photoisomerization of this construct was investigated. Irradiation with UV light (365 nm) for 30 min triggered clean isomerization of the PPV block from all-*cis* to all-*trans* as shown by 1H-NMR and UV-visible absorption spectroscopy (Figure 6). Careful inspection of the 1H-NMR spectra showed that the block based on **3** remained unchanged during the isomerization, which highlights the mildness and block-selectivity of the process. As shown by dynamic light scattering, the size of the particles increased as the coiled chain was transformed to a rod-like structure (Figure S24). As expected, the solubility of the resulting polymer was lower, as **poly-all-*cis*-3-*b*-all-*trans*-1a** precipitated out of the THF solution over time.

In summary, we disclosed the first synthesis of all-*cis* PPVs with living characteristics using a stereoretentive ROMP strategy. This process does not require the preparation of stereodefined linear alkenes or harsh conditions using stoichiometric metal reagents, and thus could be applicable to a variety of monomers.[38–40] The optimized conditions allowed for a controlled chain-growth process resulting in polymers with predicable M_n and narrow Đ values. The high-chain fidelity was harnessed to prepare block copolymers that can be isomerized with UV light. We anticipate that the efficiency and practicality of the photoisomerization combined with the universality of ROMP will allow the synthesis of all-*cis* PPVs embedded in complex polymeric architectures, and to exploit the full potential of PPV as stimuli-responsive materials.

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Acknowledgment

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