

Communication

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

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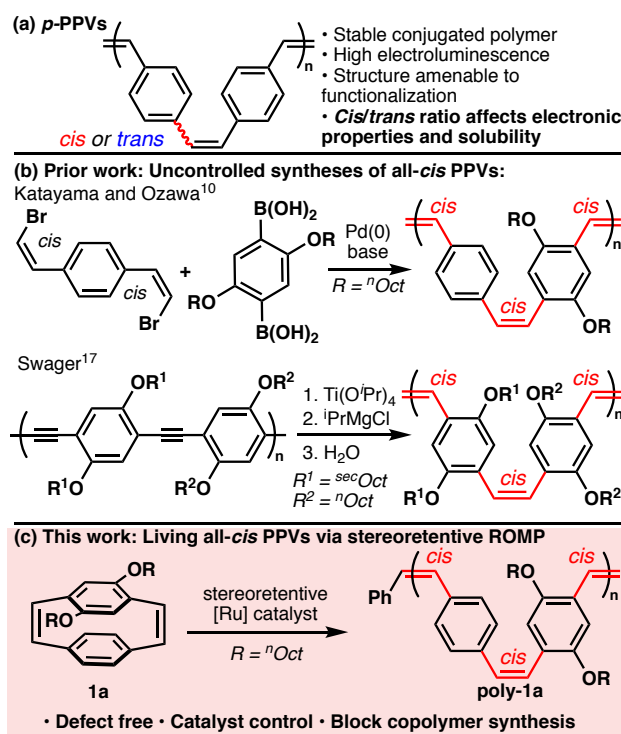
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Supporting Information Placeholder

**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 a 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 average molar masses. All-*cis* PPVs can then serve as light-responsive polymers through clean photoisomerization of the stilbenoid units.

Despite decades of study into the poly(*p*-phenylene vinylene) (PPV) family of conjugated polymers (Figure 1a), methods for the precise control of each stilbenoid olefin configuration remain scarce.<sup>1</sup> Indeed, the *cis* or *trans* (*Z* or *E*) configuration of the olefins dramatically affects the physical and chemical 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  $\pi$ - $\pi$  interactions and packing. As a result, *cis* alkenes tend to decrease the effective conjugation length of the polymer but increase its solubility.<sup>2,3</sup> PPV was used to make the first organic light-emitting diode (OLED),<sup>4</sup> and was one of the components blended into the first “bulk heterojunction” solar cells.<sup>5</sup> 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.<sup>6</sup> This effort led to many robust syntheses of PPVs, including controlled polymerizations, with high molar masses ( $M_n$ ),<sup>7,8</sup> but few allow precise control over the configuration of the repeating olefins. Additionally, one-way<sup>9</sup> photochemical isomerization rapidly transforms *cis* into *trans* linkages. This clean photoisomerization has been exploited by Katayama and coworkers to pattern PPVs,

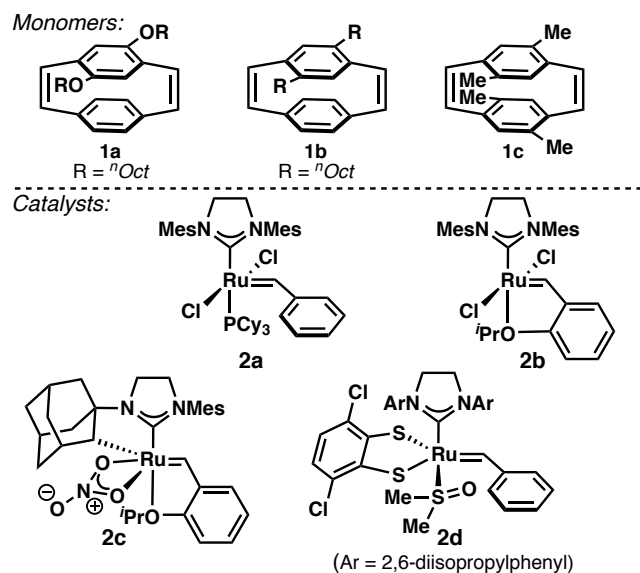
capitalizing on the difference in solubility between *cis* and *trans* congeners,<sup>10</sup> and by Choi to prepare semiconducting nanofibers via controlled self-assembly.<sup>11,12</sup> In an effort to harness the full potential of PPVs as stimuli-responsive materials, we report herein the synthesis 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,<sup>13</sup> Horner-Wadsworth-Emmons,<sup>14</sup> or Knoevenagel<sup>15</sup> 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.<sup>7,8</sup> In 2005, Katayama and coworkers reported a stereospecific Suzuki-Miyaura polymerization that affords

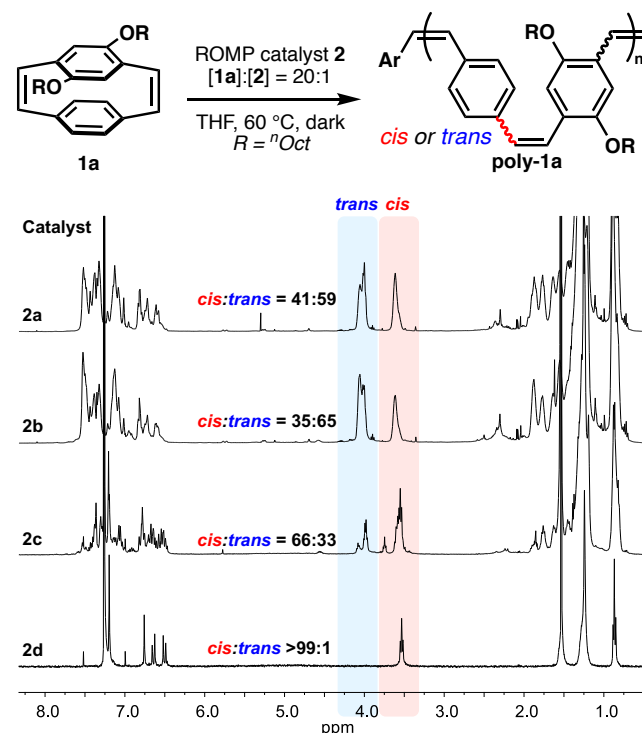
all-*cis* PPVs with low molar mass, but selectivities up to 99:1 using linear monomers with preinstalled *Z*-stereochemistry.<sup>10,16</sup> In a different approach, Swager and coworkers synthesized all-*cis* PPVs via post-polymerization reduction of poly(phenylene ethynylene)s (PPEs) with stoichiometric titanium isopropoxide and isopropyl magnesium chloride.<sup>17</sup> Both routes afforded impressive stereoselectivity, but are based on uncontrolled chain-growth polymerization, which limits their applications. Our strategy to access all-*cis* PPVs with living characteristics relied on the polymerization of [2.2] paracyclophane-1,9-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' 2<sup>nd</sup> generation catalyst (**2a**) (see Figure 2 for catalyst structures).<sup>18–20</sup> The *trans* alkenes are postulated to arise from isomerization driven by the catalyst during ROMP. We hypothesized that either *Z*-selective<sup>21</sup> or stereoretentive<sup>22–24</sup> metathesis catalysts could allow for the controlled preparation of all-*cis* PPVs with predictable high  $M_n$ 's, low  $D$ 's, and little to no *trans* defects. While *Z*-selective catalyst **2c** has been applied to polymerize a variety of norbornene derivatives,<sup>25</sup> stereoretentive dithiolate-chelated Ru catalysts such as **2d** have seldomly been used for ROMP. Only norbornene,<sup>22,26</sup> cyclooctadiene,<sup>22</sup> and norbornadiene<sup>27</sup> have been polymerized with this new generation of catalysts that enables retention of the alkene stereochemistry during metathesis.<sup>28,29</sup> Importantly, perfect *cis* control in the ROMP process was targeted since any post-polymerization isomerization would lead to all-*trans* PPVs.<sup>30–32</sup>



**Figure 2.** [2.2] Paracyclophane-1,9-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 [2.2] paracyclophane-1,9-diene monomers **1a–c** were synthesized using literature procedures

(Figure 2).<sup>19,33</sup> 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 <sup>1</sup>H-NMR spectroscopy 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 <sup>1</sup>H-NMR spectroscopy (Figure 3).<sup>10</sup> In THF at 60 °C, Grubbs' 2<sup>nd</sup> 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' 2<sup>nd</sup> 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** inverted that ratio, with 66% of the olefins being *cis*-configured. To our delight, complete *cis* selectivity (> 99:1) was observed using stereoretentive catalyst **2d** recently synthesized by Materia Inc.<sup>34</sup> Following ROMP with **2d**, no *trans* linkages could be detected in **poly-1a** within the limits of sensitivity of <sup>1</sup>H-NMR spectroscopy.



**Figure 3.** <sup>1</sup>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**.

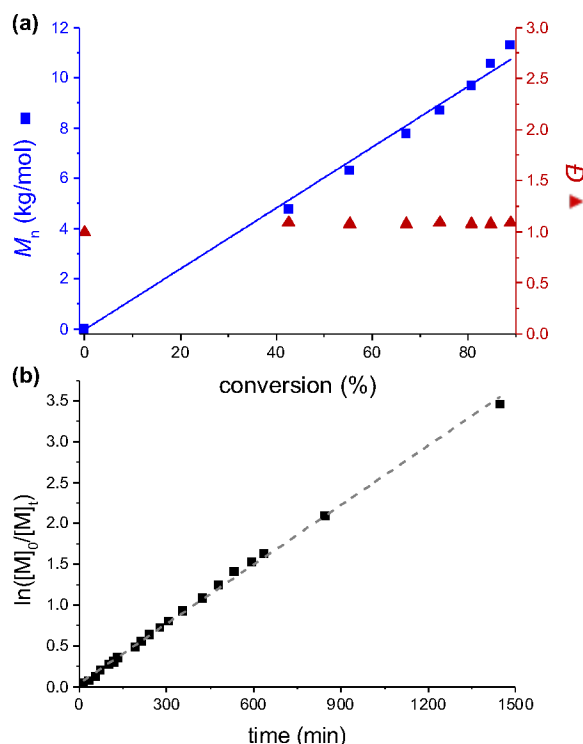
The reaction conditions using **2d** were then optimized in order to furnish PPVs with living characteristics using **2d**. Polymerizations were kept in the dark to avoid

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 13.1 kg/mol and low  $D$ '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 around 1.1 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.**

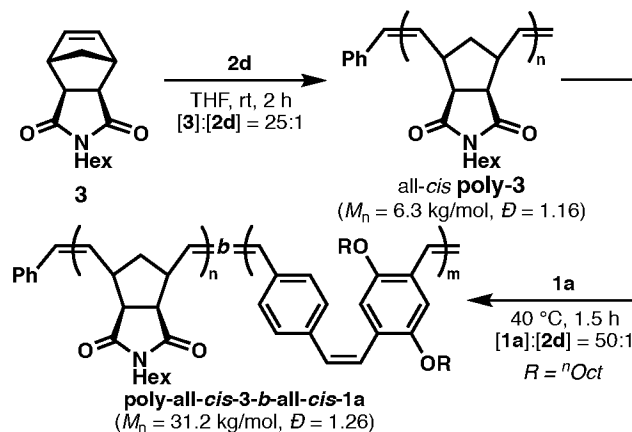
Entry <sup>a</sup>	1a:2d ratio	1a conversion	$M_n^{\text{theo}}$ (kg/mol)	$M_n^{\text{exp}}$ (kg/mol)	$D$
1	10:1	100%	4.7	5.5	1.15
2	20:1	100%	9.3	9.1	1.08
3	30:1	100%	13.9	13.1	1.11

<sup>a</sup>**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  $D$ 's were determined by SEC (THF) using polystyrene standards (RI detection).



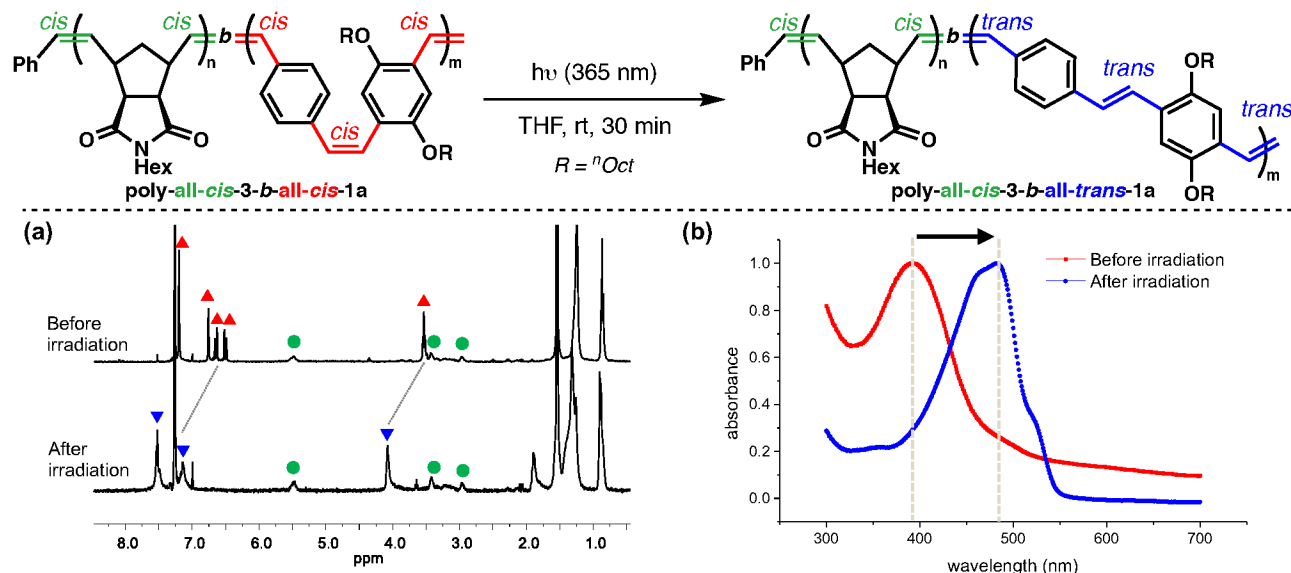
**Figure 4.** Polymerization of **1a** with catalyst **2d** at room temperature: (a)  $M_n$  and  $D$  vs conversion ( $[1a]:[2d] = 25:1$ ). (b) Determination of the rate of propagation ( $[2d] = 0.9$  mM,  $R^2 = 0.99795$ ). Kinetic studies were performed at room temperature to slow down the propagation and to allow for the collection of data points over a convenient length of time.

The living character of the polymerization process was confirmed by a first-order consumption of monomer **1a** as illustrated by the linear association between  $\ln([M]_0/[M]_t)$  and time (Figure 4b). The slope of this linear plot provided the apparent rate constant of propagation,  $k_p^{\text{app}} = 0.00243$  min<sup>-1</sup>. The rate of initiation was too high to be calculated by NMR spectroscopy 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 [2.2] paracyclophane-1,9-diene monomers.<sup>35,36</sup>



**Figure 5.** Synthesis of all-*cis* **poly-3** and **poly-all-cis-3-b-all-cis-1a** via chain extension.

By contrast to the prior syntheses of all-*cis* PPVs,<sup>10,17</sup> 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**<sup>37,38</sup> 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,<sup>22</sup> only *cis* linkages were identified in **poly-3** by NMR spectroscopy. With **poly-all-cis-3-b-all-cis-1a** in



**Figure 6.** Photoisomerization **poly-all-cis-3-b-all-cis-1a**: a) <sup>1</sup>H-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.

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 <sup>1</sup>H-NMR and UV-visible absorption spectroscopies (Figure 6). Careful inspection of the <sup>1</sup>H-NMR spectra showed that the block based on **3** remained unchanged during the isomerization, which highlights the mildness and block-selectivity of the process. Analysis of the particle size by dynamic light scattering was complicated by potential aggregation of **poly-all-cis-3-b-all-cis-1a**. A marked increase of the hydrodynamic radius was nonetheless observed after photoisomerization consistent with a coil-to-rod transition (Figure S24). As expected, the solubility of the resulting polymer was lower, as **poly-all-cis-3-b-all-trans-1a** started to precipitate out of the THF solution during irradiation.

In summary, we have demonstrated that the exquisite stereoselectivity afforded by dithiolate-chelated Ru metathesis catalysts is not limited to common norbornene-based monomers. Catalyst **2d** allows the efficient and stereoretentive ROMP of unusual [2.2] paracyclophane-1,9-diene monomer **1a**, which provides access to well-defined and functionalizable all-*cis* PPVs. This approach does not require the preparation of stereodefined linear alkenes or harsh conditions using stoichiometric metal reagents, and thus could deliver all-*cis* PPVs based on a variety of paracyclophane-type monomers.<sup>39–41</sup> The optimized conditions allowed for a controlled chain-growth process resulting in polymers with predictable  $M_n$  and narrow  $D$  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.

## ASSOCIATED CONTENT

Supporting Information.

The Supporting Information is available free of charge on the ACS Publications website.

General experimental considerations, experimental procedures, and additional supporting data (PDF).

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### Notes

The authors declare no competing financial interest.

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## REFERENCES

- (1) Blayney, A. J.; Perepichka, I. F.; Wudl, F.; Perepichka, D. F. Advances and Challenges in the Synthesis of Poly(*p*-phenylene vinylene)-Based Polymers. *Isr. J. Chem.* **2014**, *54*, 674–688.
- (2) Wang, F.; He, F.; Xie, Z.; Li, M.; Hanif, M.; Gu, X.; Yang, B.; Zhang, H.; Lu, P.; Ma, Y. A solution-processible poly(*p*-phenylene vinylene) without alkyl substitution: Introducing the *cis*-vinylene segments in polymer chain for improved solubility, blue emission, and high efficiency. *J. Polym. Sci., Part A: Polym. Chem.* **2008**, *46*, 5242–5250.
- (3) Wang, F.; He, F.; Xie, Z. Q.; Li, Y. P.; Hanif, M.; Li, M.; Ma, Y. Poly(*p*-phenylene vinylene) Derivatives with Different Contents of *cis*-Olefins and their Effect on the Optical Properties. *Macromol. Chem. Phys.* **2008**, *209*, 1381–1388.
- (4) Burroughes, J. H.; Bradley, D. D. C.; Brown, A. R.; Marks, R. N.; Mackay, K.; Friend, R. H.; Burns, P. L.; Holmes, A. B. Light-emitting diodes based on conjugated polymers. *Nature* **1990**, *347*, 539–541.
- (5) Yu, G.; Gao, J.; Hummelen, J. C.; Wudl, F.; Heeger, A. J. Polymer Photovoltaic Cells: Enhanced Efficiencies via a Network of Internal Donor-Acceptor Heterojunctions. *Science* **1995**, *270*, 1789–1791.
- (6) Grimsdale, A. C.; Leok Chan, K.; Martin, R. E.; Jokisz, P. G.; Holmes, A. B. Synthesis of Light-Emitting Conjugated Polymers for Applications in Electroluminescent Devices. *Chem. Rev.* **2009**, *109*, 897–1091.
- (7) Junkers, T.; Vandenberg, J.; Adriaensens, P.; Lutsen, L.; Vanderzande, D. Synthesis of poly(*p*-phenylene vinylene) materials via the precursor routes. *Polym. Chem.* **2012**, *3*, 275–285.
- (8) Zaquen, N.; Lutsen, L.; Vanderzande, D.; Junkers, T. Controlled/living polymerization towards functional poly(*p*-phenylene vinylene) materials. *Polym. Chem.* **2016**, *7*, 1355–1367.
- (9) Arai, T.; Tokumaru, K. Photochemical one-way adiabatic isomerization of aromatic olefins. *Chem. Rev.* **1993**, *93*, 23–39.
- (10) Katayama, H.; Nagao, M.; Nishimura, T.; Matsui, Y.; Umeda, K.; Akamatsu, K.; Tsuruoka, T.; Nawafune, H.; Ozawa, F. Stereocontrolled Synthesis and Optical Properties of All-*cis* Poly(phenylene vinylenes) (PPVs): A Method for Direct Patterning of PPVs. *J. Am. Chem. Soc.* **2005**, *127*, 4350–4353.
- (11) Shin, S.; Gu, M.-L.; Yu, C.-Y.; Jeon, J.; Lee, E.; Choi, T.-L. Polymer Self-Assembly into Unique Fractal Nanostructures in Solution by a One-Shot Synthetic Procedure. *J. Am. Chem. Soc.* **2018**, *140*, 475–482.
- (12) Shin, S.; Menk, F.; Kim, Y.; Lim, J.; Char, K.; Zentel, R.; Choi, T.-L. Living Light-Induced Crystallization-Driven Self-Assembly for Rapid Preparation of Semiconducting Nanofibers. *J. Am. Chem. Soc.* **2018**, *140*, 6088–6094.
- (13) Yang, Z.; Hu, B.; Karasz, F. E. Polymer Electroluminescence Using ac or Reverse dc Biasing. *Macromolecules* **1995**, *28*, 6151–6154.
- (14) Pfeiffer, S.; Hörhold, H.-H. Investigation of poly(arylene vinylene)s, 41. Synthesis of soluble dialkoxy-substituted poly(phenylene alkenylidene)s by applying the Horner-reaction for condensation polymerization. *Macromol. Chem. Phys.* **1999**, *200*, 1870–1878.
- (15) Morin, J.-F.; Drolet, N.; Tao, Y.; Leclerc, M. Syntheses and Characterization of Electroactive and Photoactive 2,7-Carbazolenevinylene-Based Conjugated Oligomers and Polymers. *Chem. Mater.* **2004**, *16*, 4619–4626.
- (16) Katayama, H.; Nagao, M.; Nishimura, T.; Matsui, Y.; Fukuse, Y.; Wakioka, M.; Ozawa, F. Stereocontrolled Synthesis and Characterization of *cis*-Poly(arylenevinylene)s. *Macromolecules* **2006**, *39*, 2039–2048.
- (17) Moslin, R. M.; Espino, C. G.; Swager, T. M. Synthesis of Conjugated Polymers Containing *cis*-Phenylenevinylenes by Titanium-Mediated Reductions. *Macromolecules* **2009**, *42*, 452–454.
- (18) Yu, C.-Y.; Turner, M. L. Soluble Poly(*p*-phenylenevinylene)s through Ring-Opening Metathesis Polymerization. *Angew. Chem. Int. Ed.* **2006**, *45*, 7797–7800.
- (19) Lidster, B. J.; Behrendt, J. M.; Turner, M. L. Monotelechelic poly(*p*-phenylenevinylene)s by ring opening metathesis polymerisation. *Chem. Commun.* **2014**, *50*, 11867–11870.
- (20) Lidster, B. J.; Kumar, D. R.; Spring, A. M.; Yu, C.-Y.; Turner, M. L. Alkyl substituted poly(*p*-phenylene vinylene)s by ring opening metathesis polymerisation. *Polym. Chem.* **2016**, *7*, 5544–5551.
- (21) Herbert, M. B.; Grubbs, R. H. Z-Selective Cross Metathesis with Ruthenium Catalysts: Synthetic Applications and Mechanistic Implications. *Angew. Chem. Int. Ed.* **2015**, *54*, 5018–5024.
- (22) Khan, R. K. M.; Torker, S.; Hoveyda, A. H. Readily Accessible and Easily Modifiable Ru-Based Catalysts for Efficient and Z-Selective Ring-Opening Metathesis Polymerization and Ring-Opening/Cross-Metathesis. *J. Am. Chem. Soc.* **2013**, *135*, 10258–10261.
- (23) Montgomery, T. P.; Ahmed, T. S.; Grubbs, R. H. Stereoretentive Olefin Metathesis: An Avenue to Kinetic Selectivity. *Angew. Chem. Int. Ed.* **2017**, *56*, 11024–11036.
- (24) Müller, D. S.; Baslé, O.; Mauduit, M. A tutorial review of stereoretentive olefin metathesis based on ruthenium dithiolate catalysts. *Beilstein J. Org. Chem.* **2018**, *14*, 2999–3010.
- (25) Keitz, B. K.; Fedorov, A.; Grubbs, R. H. *Cis*-Selective Ring-Opening Metathesis Polymerization with Ruthenium Catalysts. *J. Am. Chem. Soc.* **2012**, *134*, 2040–2043.
- (26) Wang, T.; Wu, B.; Guo, W.; Wu, S.; Zhang, H.; Dang, Y.; Wang, J. Synthesis, catalysis, and DFT study of a ruthenium carbene complex bearing a 1,2-dicarbadodecaborane (12)-1,2-dithiolate ligand. *Dalton Trans.* **2019**, *48*, 2646–2656.
- (27) Mikus, M. S.; Torker, S.; Hoveyda, A. H. Controllable ROMP Tacticity by Harnessing the Fluxionality of Stereogenic-at-Ruthenium Complexes. *Angew. Chem. Int. Ed.* **2016**, *55*, 4997–5002.
- (28) While this manuscript was under review, an elegant study expanding the monomer scope of stereoretentive ROMP was reported: Song, J.-A.; Peterson, G. I.; Bang, K.-T.; Ahmed, T. S.; Sung, J.-C.; Grubbs, R. H.; Choi, T.-L. Ru-Catalyzed, *cis*-Selective Living Ring-Opening Metathesis Polymerization of Various Monomers, Including a Dendronized Macromonomer, and Implications to Enhanced Shear Stability. *J. Am. Chem. Soc.* **2020**, *142*, 10438–10445.
- (29) Dithiolate-chelated Ru catalysis have also been used to obtain regioselectivity in the cyclopolymers of diynes. See a) Jung, H.; Jung, K.; Hong, M.; Kwon, S.; Kim, K.; Hong, S. H.; Choi, T.-L.; Baik, M.-H. Understanding the Origin of the Regioselectivity in Cyclopolymers of Diynes and How to Completely Switch It. *J. Am. Chem. Soc.* **2018**, *140*, 834–841; b) Jung, K.; Kim, K.; Sung, J.-C.; Ahmed, T. S.; Hong, S. H.; Grubbs, R. H.; Choi, T.-L. Toward Perfect Regiocontrol for  $\beta$ -Selective Cyclopolymers Using a Ru-Based Olefin Metathesis Catalyst. *Macromolecules* **2018**, *51*, 4564–4571.
- (30) Conticello, V. P.; Gin, D. L.; Grubbs, R. H. Ring-opening metathesis polymerization of substituted bicyclo[2.2.2]octadienes: a new precursor route to poly(1,4-phenylenevinylene). *J. Am. Chem. Soc.* **1992**, *114*, 9708–9710.

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- (31) Miao, Y.-J.; Bazan, G. C. Paracyclophane Route to Poly(*p*-phenylenevinylene). *J. Am. Chem. Soc.* **1994**, *116*, 9379–9380.
- (32) Wagaman, M. W.; Grubbs, R. H. Synthesis of Organic and Water Soluble Poly(1,4-phenylenevinylenes) Containing Carboxyl Groups: Living Ring-Opening Metathesis Polymerization (ROMP) of 2,3-Dicarboxybarrelenes. *Macromolecules* **1997**, *30*, 3978–3985.
- (33) Lidster, B. J.; Kumar, D. R.; Spring, A. M.; Yu, C.-Y.; Helliwell, M.; Raftery, J.; Turner, M. L. Alkyl substituted [2.2]paracyclophane-1,9-dienes. *Org. Biomol. Chem.* **2016**, *14*, 6079–6087.
- (34) Johns, A. M. Synthesis and characterization of metathesis catalysts. Patent WO2018038928A1, August 10, 2017.
- (35) Kumar, D. R.; Lidster, B. J.; Adams, R. W.; Turner, M. L. Mechanistic investigation of the ring opening metathesis polymerisation of alkoxy and alkyl substituted paracyclophanedienes. *Polym. Chem.* **2017**, *8*, 3186–3194.
- (36) Menk, F.; Mondeshki, M.; Dudenko, D.; Shin, S.; Schollmeyer, D.; Ceyhun, O.; Choi, T.-L.; Zentel, R. Reactivity Studies of Alkoxy-Substituted [2.2]Paracyclophane-1,9-dienes and Specific Coordination of the Monomer Repeating Unit during ROMP. *Macromolecules* **2015**, *48*, 7435–7445.
- (37) Matson, J. B.; Grubbs, R. H. Synthesis of Fluorine-18 Functionalized Nanoparticles for use as in vivo Molecular Imaging Agents. *J. Am. Chem. Soc.* **2008**, *130*, 6731–6733.
- (38) Cole, J. P.; Lessard, J. J.; Lyon, C. K.; Tuten, B. T.; Berda, E. B. Intra-chain radical chemistry as a route to poly(norbornene imide) single-chain nanoparticles: structural considerations and the role of adventitious oxygen. *Polym. Chem.* **2015**, *6*, 5555–5559.
- (39) Mäker, D.; Bunz, U. H. F. Fourfold Alkoxy-Substituted [2.2.2]Paracyclophane-1,9,17-trienes–ROMP into PPVs with Unusual Topologies. *Macromol. Rapid Commun.* **2014**, *35*, 2096–2100.
- (40) Elacqua, E.; Weck, M. Fabrication of Supramolecular Semiconductor Block Copolymers by Ring-Opening Metathesis Polymerization. *Chem. Eur. J.* **2015**, *21*, 7151–7158.
- (41) Elacqua, E.; Gregor, M. Poly(arylenevinylene)s through Ring-Opening Metathesis Polymerization of an Unsymmetrical Donor-Acceptor Cyclophane. *Angew. Chem. Int. Ed.* **2019**, *58*, 9527–9532.

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