Cyclophanediene and Cyclophanetriene-Based Conjugated Polymers

*Arielle Mann, Matthew D. Hannigan, and Marcus Weck**

Department of Chemistry and Molecular Design Institute, New York University, New York, NY 10003, USA

Keywords: [2.2]Paracyclophane-1,9-diene, Ring-opening metathesis polymerization, poly(*p*-phenylene vinylene), block copolymer, Grubbs catalyst

Abstract:

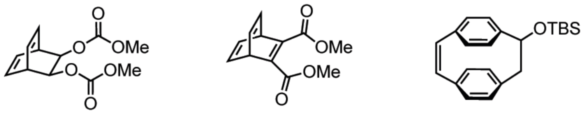
Poly(*p*-phenylene vinylene)s (PPVs) and poly(arylene vinylene)s are key materials for a variety of applications ranging from organic light emitting diodes to fluorescent optical probes. Their syntheses, however, have been hampered by non-living or step-growth polymerization techniques. The development of functional-group tolerant olefin metathesis catalysts has enabled the use of living ring-opening metathesis polymerization (ROMP) of cyclophane monomers yielding PPVs and poly(*p*-phenylene-*co*-arylene vinylene)s in a living manner. Low dispersity and soluble PPVs are afforded with control over the number of repeat units with easy incorporation of different end-groups at their heads or tails. In this review, a comprehensive overview of tetrasubstituted and disubstituted alkyl and alkoxy containing [2.2]paracyclophane-1,9-diene, [2.2]metaparacyclophane-1,9-diene, [2.2.2]paracyclophane-1,9,17-triene, and benzothiadiazole-[2.2]paracyclophane-1,9-diene is provided. The high ring strain of these monomers enables efficient polymerizations with ruthenium initiators. A particular emphasis is on [2.2]paracyclophane-1,9-dienes as it is the most investigated class of polymerized cyclophanediene since initially reported 30 years ago. Additionally, applications for soft materials synthesized by ROMP are examined, highlighting easily accessed PPV copolymers and PPV block

copolymers that can be phototriggered, as well as PPVs featuring supramolecular recognition units installed at their termini to afford orthogonally self-assembled architectures.

1. Introduction

The discovery of poly(acetylene)'s conductive properties in the 1970's launched the field of π-conjugated polymers for semiconducting materials.[1] Of the many types of conjugated polymers,[2-3] poly(*p*-phenylene vinylene) (PPV) is among the most interesting material due to the simplicity of its structure (alternating arylene and olefin repeating units) and its band gap being in the visible region.[4] As one of the earliest air-stable conjugated polymer investigated, it was applied as the active layer of the first organic light emitting diode (OLED).[5] Deemed a workhorse of organic semiconductors,[6] the electroluminescent properties of PPVs have been the subject of multiple reviews.[4, 7-11] While the use of PPVs as sensors[12] and in optoelectronic purposes has declined over the past two decades to make way for higher performing organic-photovoltaic materials,[3, 13-14] applications utilizing their excellent fluorescent properties continue to be explored, especially in the biomedical field.[15-25] Despite the attention PPVs have drawn, challenges to their synthesis have plagued the development of PPV-based materials.

As a rigid-rod polymer, unsubstituted PPVs are insoluble in most solvents, therefore, the development of solution processable PPVs has been a target. Common methods for PPV fabrication are well reviewed and include "precursor routes", such as the Wessing route or the Gilch polymerization, which involve depositing soluble precursors to generate PPVs.[11, 26-28] Non-precursor routes involve soluble small molecules that can generate polymers include step-growth polymerizations using carbon-carbon bond formations such as the Wittig reaction or palladium-catalyzed coupling reactions including the Heck, the Stille, or the Suzuki reactions.[11, 26, 29-31] While these methods successfully afford PPVs, they are not living chain-growth polymerizations and mainly yield oligomers or low molecular weight polymers. As such, these methods do not enable control over the molecular weight, nor do they allow for the formation of block copolymers and instead give polymers with high dispersity, incorporating significant backbone defects. These shortcomings negatively affect the optoelectronic properties of PPV-based materials, evidenced by comparison studies showing that devices made from PPVs with narrow dispersities and less regiodefects have improved optical properties.[11, 32] This improvement in properties with regioregularity and dispersity demonstrates the necessity to develop synthetic strategies towards PPVs that enable control over molecular weight and dispersity, i.e., via living chain-growth polymerization.

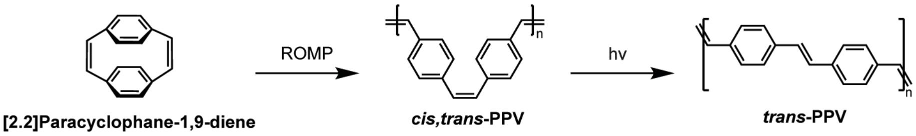


Bicyclo[2.2.2]octadiene **Bicyclo[2.2.2]octatriene** **[2.2]Paracyclophane-1-ene**

Figure 1. Structures of monomers previously used in the ring-opening metathesis polymerizations to afford PPV.

The controlled anionic and radical polymerizations of quinodimethane monomers using a sulfinyl precursor route have been reported,[33] as well as the use of olefin metathesis polymerizations: acyclic diene metathesis (ADMET) and ring-opening metathesis polymerizations (ROMP, a living polymerization) to afford PPVs.[34-35] Early reported monomers that can be ring-opened to PPVs include bicyclo[2.2.2]octadiene,[36] bicyclo[2.2.2]octatriene (also known as barrelene),[37] and [2.2]paracyclophan-1-ene (**Figure 1**).[38] After polymerization, these polymers require chemical or thermolytic conversion to form PPV, which can result in backbone defects. Additionally, these methods result in insoluble PPVs as they lack solubilizing side-chains on the benzene repeat units, preventing use in some applications. Alternatively, [2.2]paracyclophane-1,9-

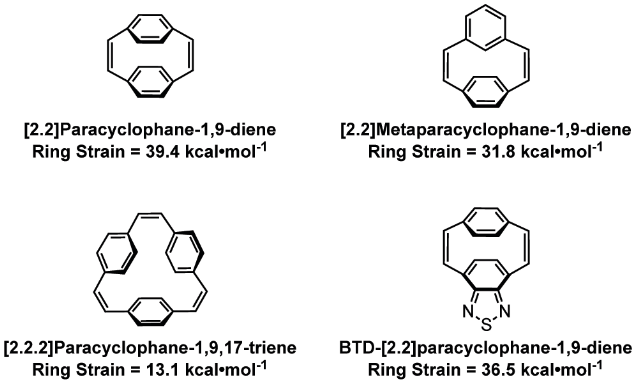
diene (pCpd) is a monomer that can be polymerized via ROMP to afford soluble, low dispersity PPVs without requiring potentially destructive post-polymerization modifications to afford the target conjugated polymer. Due to the unique structure of pCpd, once ring-opened the alkene stereochemistry of the PPV is controlled and can be photoisomerized to the all-*trans*-PPV which may be favorable in some applications for their narrower band gaps (**Scheme 1**).[11]



Scheme 1. General reaction scheme for the ring-opening metathesis polymerization of [2.2]paracyclophane-1,9-diene and its photoisomerization.

This review covers the synthesis of substituted cyclophanedienes and related cyclophanetrienes monomers as well as their reactivity with olefin metathesis catalysts since their first report 30 years ago. The focus will be on the living polymerization of pCpd, [2.2]metaparacyclophane-1,9-dienes, [2.2.2]paracyclophane-1,9,17-trienes, and benzothiadiazole-[2.2]paracyclophane-1,9-dienes (**Figure 2**) to afford well-defined poly(phenylene vinylene)s and poly(*p*-phenylene-*co*-arylene vinylene)s with particular emphasis on the synthesis and polymerization of the most investigated class of cyclophanediene, pCpd. The advantages of using ROMP to access conjugated polymers from olefin-containing cyclophanes will be summarized, highlighting optoelectronic property control and applications into fluorescent and phototriggerable materials.

2. Synthesis of Cyclophane Monomers



[2.2]Paracyclophane-1,9-diene
Ring Strain = 39.4 kcal•mol^{-1}

[2.2]Metaparacyclophane-1,9-diene
Ring Strain = 31.8 kcal•mol^{-1}

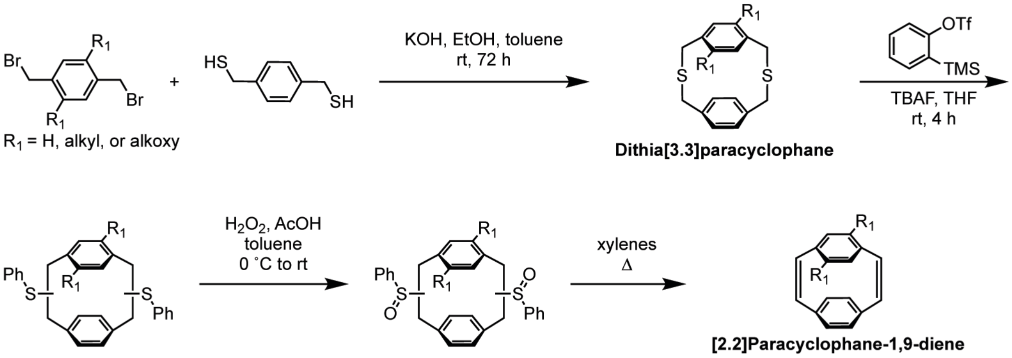
[2.2.2]Paracyclophane-1,9,17-triene
Ring Strain = 13.1 kcal•mol^{-1}

BTD-[2.2]paracyclophane-1,9-diene
Ring Strain = 36.5 kcal•mol^{-1}

Figure 2. Structures of [2.2]paracyclophane-1,9-diene, [2.2]metaparacyclophane-1,9-diene, [2.2.2]paracyclophane-1,9,17-triene, and benzothiadiazole-[2.2]paracyclophane-1,9-diene. Their ring strain energies were calculated via density functional theory at the M11/6-311G*//M11/6-31G* level of theory (see the supporting information). BTD = 2,1,3-benzothiadiazole

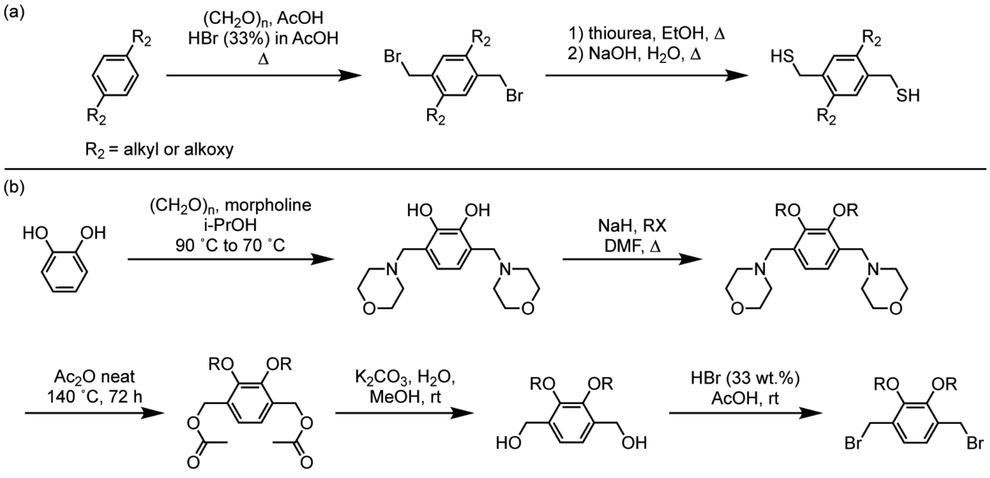
2.1 [2.2]Paracyclophane-1,9-diene (pCpd)

Dewhirst and Cram first reported the synthesis of pCpd in 1958 from [2.2]paracyclophane with a meager 14% yield due to the harsh reaction conditions required.[39] Since then, a more practical and higher yielding scheme for the synthesis of pCpd was devised by Boekelheide and coworkers (**Scheme 2**).[40-41] Starting with a bis(bromomethyl)benzene and a bis(methylenethiol)benzene, the two aromatic building blocks are slowly combined (over a period of days) at low concentrations to afford dithia[3.3]paracyclophane. These low concentrations are required to favor the intramolecular reaction between the methylenethiol and the bromomethyl groups to form the dithia[3.3]paracyclophane; higher concentrations favor the intermolecular reaction, generating undesired linear oligomeric side products. A ring contraction to afford the bis(sulfide)-[2.2]paracyclophane is accomplished using a benzyne-induced Stevens rearrangement. Subsequent oxidation generates the corresponding bis(sulfoxide), which is thermally eliminated to afford the pCpd (Scheme 2).[41-43] If a *meta*-bis(bromomethyl)benzene is used, the corresponding [2.2]metaparacyclophane-1,9-diene is formed.[44-45] However, if both the bis(bromomethyl)benzene and the bis(methylenethiol) are *meta* substituted, pyrene results from the thermal elimination of the sulfoxide, rather than the cyclophanediene.[41] A similar scheme for the ring contraction utilizing the Pummerer rearrangement has been reported for synthesizing pCpds but it has not been widely applied.[46] Additionally, other alkene-forming reactions such as the Ramberg-Bäcklund, McMurry, and Wittig reactions have been attempted for synthesizing pCpd have failed to result in the desired highly-strained cyclophanediene.[47] A Wittig reaction is successful, however, at forming the less strained all-*ortho* (5*Z*,11*E*)-dibenzo[*a*,*e*]cyclooctatetraene which can also be polymerized via ROMP.[48]



Scheme 2. Common synthetic route for [2.2]paracyclophane-1,9-dienes.

From a physical-organic perspective, pCpd is a remarkable compound due to the high strain inherent in its structure. In pCpd, the location of the ethylene "bridges" prevents the molecule from being planar. Instead, the benzene rings are forced to adopt a face-to-face eclipsed (or "sandwich stack") conformation. Due to this geometry, pCpds have a high ring strain, evidenced by the crystal structure of unsubstituted pCpd showing the benzene rings are bent 15° out of plane at each bridgehead carbon, causing the benzenes to form a boat-like structure.[49] pCpds, additionally, have strain due to the repulsion of π-orbitals between the benzene rings,[50-51] given the smaller centroid-to-centroid distance (3.14 Å) separating the benzenes rings compared to sandwich-stacked benzene dimers (~3.7-4.0 Å).[50] As a result, the strain energy of these "bent and battered benzene rings"[52] for unsubstituted pCpd has previously been determined to be 42.0 kcal•mol^{-1} close to our own density functional theory (DFT) calculations which determined it to be 39.4 kcal•mol^{-1} (**Figure 2**). This high strain energy makes pCpds ideal monomers for living ROMP.[53]



Scheme 3. General synthetic route for making side-chain incorporated starting materials for [2.2]paracyclophane-1,9-dienes.

With established methods for synthesizing the pCpd skeleton, incorporating solubilizing side-chains in both the *para* and *ortho* positions has been accomplished, enabling a diverse library of pCpds that can be used as monomers for ROMP. When side-chains are incorporated, planar chiral pCpd enantiomers form: R_p and S_p.[54] Given that enantiomers have the same chemical reactivity with achiral compounds, both enantiomers are reactive in ROMP with achiral ruthenium catalysts. All monomers discussed in this review are prepared and used as a mixture of the planar chiral enantiomers.

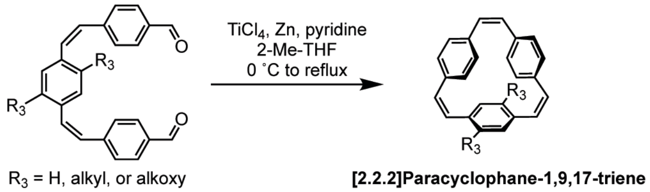
An early method of incorporating alkoxy side-chains involved a photooxygenation reaction with pCpd to afford a substitutable hydroquinone cyclophane scaffold.[55-57] While this method can be useful, substituted pCpds are commonly synthesized via a "bottom-up" method developed by the Turner group, so named because the benzenes are substituted before cyclization into a cyclophane. Beginning with *para*-dialkyl or *para*-dialkoxy benzenes, treatment with paraformaldehyde and the commercially available 33 wt% solution of hydrobromic acid in acetic acid results in *para*-bis(bromomethyl)benzene.[42-43] These bromomethyl side-chains can also be converted into the bis(methylenethiol)benzene by treatment with thiourea (**Scheme 3a**). To access pCpds with *ortho*-alkoxy side-chains, an altered strategy is used as reported by our group.[58] The key step to synthesizing the *2,3*-alkoxy-1,4-bis(bromomethyl)benzene takes advantage of the Mannich reaction with phenols to incorporate bis(morpholinomethyl) groups *para* to each other which is later converted to the bis(bromomethyl)benzene (**Scheme 3b**).

Substitution pattern affects the electronic properties of the polymer, and endows the PPV different optical properties based on the position and type of side-chain that is incorporated (*vide infra*).[11] To date, however, side-chain diversity of pCpds that have been polymerized is limited to alkyl or alkoxy side-chains (with one exception by Yu *et al.* who added a tetraphenylethylene moiety).[59-60] As such, expanding methods for preparing pCpds and, as a result, the library of pCpd monomers will enable advanced applications in conjugated materials.

2.2 [2.2.2]Paracyclophane-1,9,17-triene (pCpt)

Other cyclophane monomers that have been used for ROMP are the ring-expanded derivatives of [2.2]paracyclophane-1,9-diene: the three benzene, three alkene analogue, [2.2.2]paracyclophane-1,9,17-triene (pCpt). Originally reported by Cram and coworkers,[61] structural characteristics of pCpt are similar to pCpd, in that the benzene rings are not coplanar due to steric interactions, hindering their conjugation or *global* aromaticity. Crystal structures show that two of the benzene rings are near coplanar while the third is essentially perpendicular to the plane resulting in a symmetry group of C_2 rather than D_{3h}.[62]

As the macrocycle in pCpt is larger and more flexible compared to pCpd, mild conditions can be used to synthesize it. Specifically, all-*cis* non-cyclic tri(phenylene vinylene)s can be achieved via Wittig chemistry (for the unsubstituted species)[62] or Sonogashira-Hagihara coupling (for alkyl or alkoxy functionalized benzenes) followed by a Grignard reduction [63-64] to afford the dialdehyde starting material. An intramolecular McMurry reaction is then successful to afford the desired triene (**Scheme 4**).



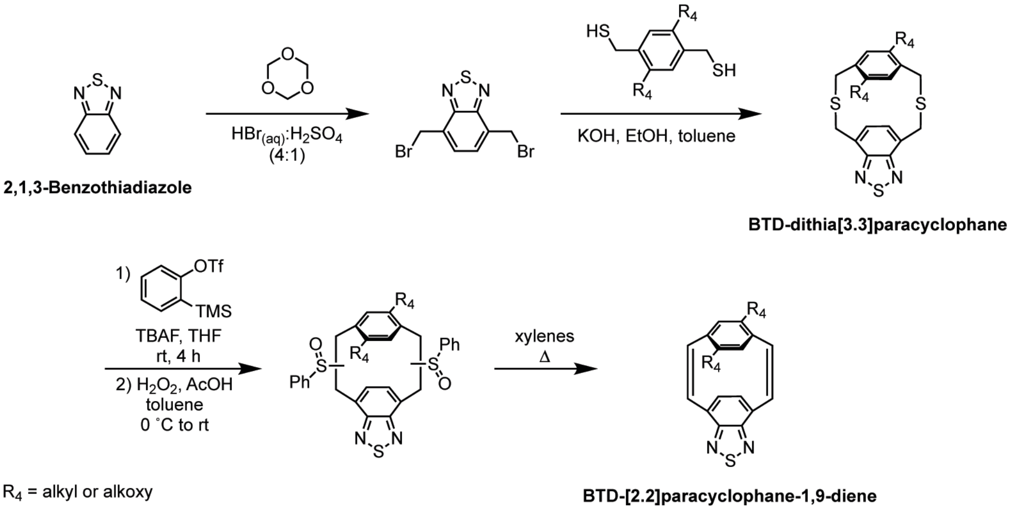
Scheme 4. General synthetic route for the formation of [2.2.2]paracyclophane-1,9,17-triene.

Using DFT calculations, we determined the strain energy of the unsubstituted pCpt to be 13.1 kcal•mol^{-1}, much lower than that of pCpd (39.4 kcal•mol^{-1}) (**Figure 2**). This difference in strain between the pCpd and pCpt indicates that living, chain-growth polymerization of pCpts is, in principle, more difficult to access given the lower driving force for ring-opening.

2.3 Benzothiadiazole-[2.2]paracyclophane-1,9-diene (BTD-pCpd)

2,1,3-Benzothiadiazole (BTD) is an electron deficient aromatic heterocyclic compound that can be incorporated into cyclophanediene. The resulting benzothiadiazole-[2.2]paracyclophane-1,9-diene (BTD-pCpd) creates an unsymmetric donor-acceptor cyclophane, adding polarization to the olefins. First reported independently by both Elacqua *et al.* and the Turner group, the synthesis of BTD-pCpd (**Scheme 5**) is similar to that of pCpd (**Schemes 2** and

3).[65-66] Beginning with BTD, the two-fold bromomethylation reaction occurs in one step using trioxane in an aqueous hydrobromic acid solution.[67] The resulting 4,7-bis(bromomethyl)benzothiadiazole can then, in principle, be combined with any dithiol previously discussed to form the BTD-dithia[3.3]paracyclophane, and converted into the diolefin in the same manner using a benzyne-induced Stephens rearrangement followed by oxidation and thermal elimination.



Scheme 5. General synthetic route for benzothiadiazole-[2.2]paracyclophane-1,9-diene. BTD = 2,1,3-benzothiadiazole

While pCpd and BTD-pCpd are geometrically similar, the different electronic character of the two arenes in the BTD containing pCpd causes differences in the strain energy of the two cyclophanedienes. Using DFT calculations, we determined the strain energy of the unsubstituted BTD-pCpd to be 36.5 kcal•mol^{-1} while the strain energy of pCpd was 39.4 kcal•mol^{-1} (**Figure 2**). We rationalize this difference primarily to the more favorable donor-acceptor interactions between the benzene and the BTD units compared to that in the benzene/benzene interactions previously discussed. Additionally, there is a lower energetic cost to deforming the benzothiadiazole, as it is a fused aromatic ring system, compared to the bending of the benzene rings. For more details, including an energy decomposition analysis of the strain energy, see the supporting information.

3. Ring-Opening Metathesis Polymerization of Cyclophanedienes and Cyclophanetrienes to Afford Poly(phenylene vinylene)s

The first ring-opening metathesis polymerization of pCpd to yield PPV was reported by Thorn-Csányi in 1992 using a tungsten olefin metathesis catalyst.[68] The pCpd monomer used by Thorn-Csányi did not bear any side-chains (and no such pCpd with alkyl and alkoxy side-chains would be reported until 2006),[69] and the resulting PPVs lacked solubility. To achieve a more processable polymer, Thorn-Csányi copolymerized pCpd with other cyclic olefins such as cyclopentene,[68, 70] 1,5-cyclooctadiene,[71] and cyclooctene.[72] Despite this strategy, the resulting polymers were not fully conjugated and still had limited solubility; polymers containing just 5% of the pCpd were isolated as an insoluble yellow material.[68] Given the limited applications of such materials with low solubility and limited conjugation, Thorn-Csányi *et al.* continued their work with PPVs synthesized by the ADMET of substituted divinylbenzenes to afford soluble PPV.[73-77] Similarly, this review focuses on di- or tetra- alkyl and alkoxy-substituted cyclophane monomers, which result in solution processible PPVs. The substitution pattern and chemical identity of the side-chains affects PPV properties. The characterization data of reported PPVs and their optical properties are summarized in **Table 1**.

Cyclophane	Polymer	DP	Đ	λ abs. max. (nm) solution1)	λ em. max. (nm) solution	Reference
[2.2]Paracyclophane-1,9-diene	**P1**	20	1.19	496	557	[69]
	P2	20	1.18	444	550	[78]
	P3	20	1.13	419	525	[58]
	P4	20	1.51	464	527, 566	[44]
	P8	20	1.40	372	491	[79]
	P9	20	1.21	371	482	[79]
[2.2]Metaparacyclophane-1,9-diene	**P7**	20	1.30	315, 397	495, 525	[44]

[2.2.2]Paracyclophane-1,9,17-triene	**P10**	52	1.9	479	539	[64]
	P11	50	1.9	484	543	[64]
	P12	50	1.4	466	517	[63]
	P13	50	1.7	453	529	[63]
	P14	6	1.9	444	502,528	[63]

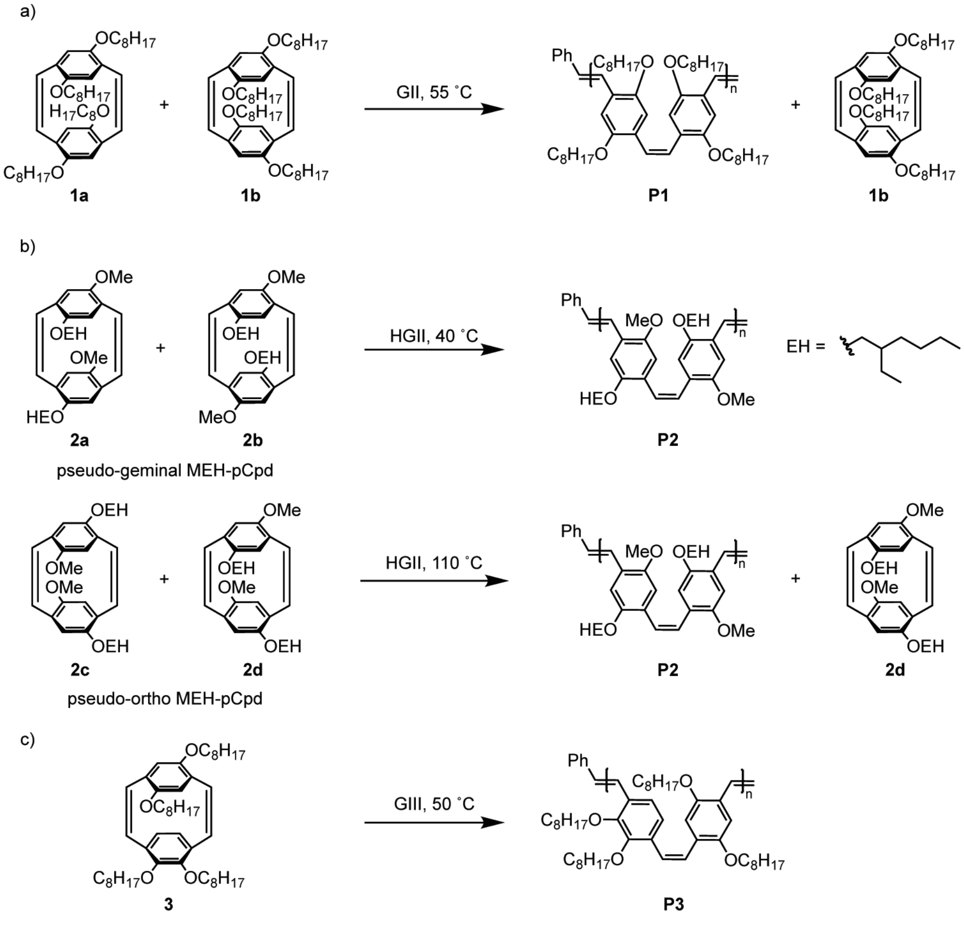
Table 1. Summary of the optical properties of PPVs synthesized by ROMP of cyclophanedienes and cyclophanetrienes [a)] absorbance reported of the *cis,trans* polymer prior to photoisomerization.

3.1 ROMP of Tetraalkoxy [2.2]Paracyclophane-1,9-diene

ROMP of tetraalkoxy pCpds (i.e., pCpds with 2 alkoxy units per benzene) gives rise to PPVs in which each benzene in the polymer has two side-chains, a structural feature which is crucial for enabling polymer solubility. While increasing the solubility is advantageous, understanding the reactivity of tetrasubstituted-pCpds towards ROMP is more complicated than for other pCpds due to the formation of diastereomers which have different steric environments around the olefins and thus, different reactivity (**Scheme 6**).

Turner and coworkers synthesized the tetraoctyloxy pCpd **1a** and **1b** consisting of two *para*-octyloxybenzenes that result in two diastereomers: the pseudo-geminal isomer **1a** where the alkoxy chains are in an eclipsed-like configuration and the pseudo-ortho isomer **1b** with staggered alkoxy side-chains in a 4:5 diastereomeric ratio. When the diastereomers are exposed to the second generation Grubbs catalyst (GII) only the pseudo-geminal monomer **1a** (the minor of the two) reacts (Scheme 6a).[42, 69] This can be attributed to the fact that olefin metathesis catalysts are very sensitive to steric hindrance.[80] The *n*-octyloxy side-chains in the pseudo-ortho isomer **1b** make both faces of both olefins sterically encumbered, blocking the ruthenium catalyst from approaching, precluding formation of the metallacyclobutane intermediate. Pseudo-geminal isomer **1a**, however, features olefins where only one face is blocked by the *n*-octyloxy side-chains, enabling ROMP with the bulky ruthenium catalyst. Polymerization was conducted with **1a** forming

P1, confirming the living nature of its ROMP. The polymer's molecular weight varied as a function of the monomer/catalyst ratio and had the expected phenyl/vinyl end-groups, consistent with a living ROMP. Additionally, the resulting *cis,trans*-PPVs were easily photoisomerized to the all-*trans*-PPV using UV light (**Scheme 1**).[69] This work was the first to use substituted pCpd-based monomers to afford soluble PPVs with low dispersity as well as control over their molecular weights and end-groups.



Scheme 6. Ring-opening metathesis polymerization of tetraalkoxy-[2.2]paracyclophane-1,9-diene monomers to their respective PPVs. EH = 2-ethylhexyl

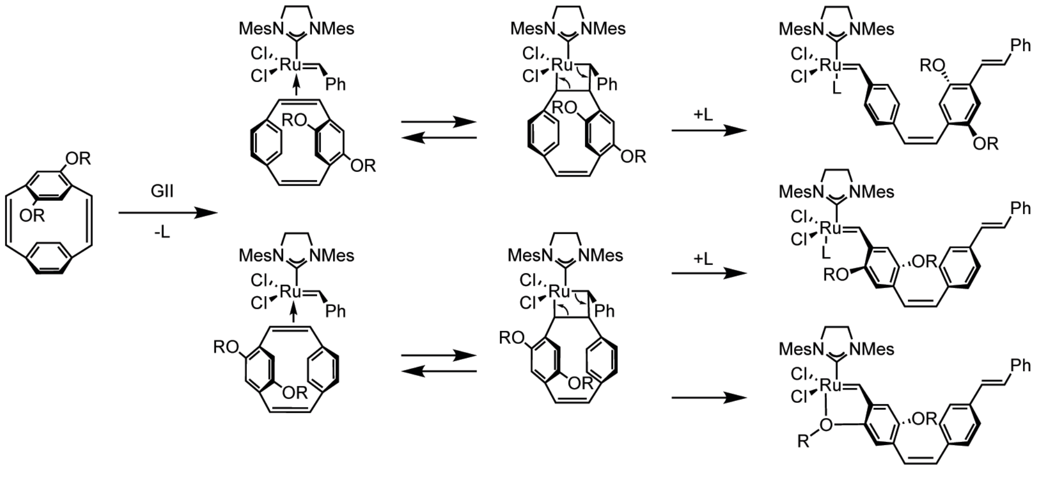
MEH-PPV (**P2**), in which one solubilizing side-chain is a methoxy group while the other is a 2-ethylhexyloxy group, is the most studied PPV.[4,11] The incorporation of a branched alkyl side-chain breaks up aggregation of the polymer's rigid-rod conjugated backbone, enabling solution processing.[4] In 2009, Turner and coworkers expanded their tetraalkoxy pCpds strategy to incorporate 2-methoxy-5-(2-ethylhexyloxy)benzene, enabling the synthesis of **P2** via ROMP. The polymerization of **2b** proceeded using Grubbs' third generation initiator, GIII, in microwave-assisted ROMP at 80 ˚C in dichloroethane.[78] Zentel and coworkers further examined **2b** as well as the three other isomers of the MEH-pCpd, **2a**, **2c**, and **2d**. They found that the other diastereomer of the MEH pseudo-geminal pCpd, **2a**, is easily ring-opened at 40 ˚C using Hoveyda-Grubbs' second generation catalyst (HGII). They went on to show, however, that when harsher conditions are used, pseudo-ortho MEH **2c** (where both methoxy groups are proximal to the same olefin) can react with the olefin metathesis catalyst in refluxing toluene while **2d** remains unreactive (Scheme 6b).[81]

The authors further examined the polymerizations of the MEH-pCpds using *in-situ* ^{1}H NMR spectroscopy to monitor the alkylidene proton's signal of the ruthenium catalyst during the propagation. They found that the oxygens from the alkoxy side-chains coordinate to the catalyst (**Scheme 7**). Thus, every polymerization step requires re-initiation, similar to that of Hoveyda-Grubbs' type catalysts.[81] This re-initiation is a slow process and thus explains why the polymerization of tetraalkoxy-substituted pCpds require heat and are generally slower (i.e. six hours/monomer)[42] compared to less strained, cyclic monomers such as norbornenes. While this coordination slows turnover, it also enhances catalyst stability, leading to less degradation under harsher reaction conditions. Thus, the higher temperatures required to ring-open the more sterically hindered monomers can be used while still managing to provide low dispersity polymers via living chain-growth polymerization.

Finally, the most recent tetraalkoxy-pCpd that has been reported is an *ortho*-*para* substituted tetraalkoxy pCpd reported by our group. Starting with an *ortho*-octyloxy substituted dibromide and a *para*-octyloxy substituted dithiol, pCpd **3** was formed in four steps. This *ortho*-*para*-tetraalkoxy pCpd monomer is advantageous compared to other tetraalkoxy-pCpd monomers that feature only *para*-alkoxy groups in that **3** only forms the planar chiral enantiomers, rather than diastereomers. The result is that, unlike previously discussed tetraalkoxy pCpds, all of the tetraalkoxy-pCpd afforded from the *ortho*-*para*-pCpd (**3**) synthesis can be polymerized via ROMP. Using GIII, **3** polymerized in a living fashion to afford copolymer **P3** (Scheme 6c). Notably, this polymer has distinct properties compared to other PPVs discussed in this section – the incorporation of an *ortho*-substituted benzene causes the fluorescence of the PPV to be blue-shifted compared to its all-*para* PPV counterparts (Table 1).[58] In the future, utilizing a combination of *ortho*-*para*- and all-*para* pCpds could provide a strategy to tune the optical properties of PPVs for specific applications.

3.2 ROMP of Dialkoxy [2.2]Paracyclophane-1,9-diene

Tetraalkoxy-pCpds have long polymerization times and limited reactivity due to diastereoselectivity, inspiring investigations into other types of alkoxy-substituted pCpd monomers – particularly dialkoxy-substituted pCpds. While the ROMP of dialkoxy-pCpds results in half as many alkoxy side-chains in the resulting PPV, dialkoxy-PPVs still show good solubility in a variety of solvents. The decrease in the number of these solubilizing groups, therefore, is not detrimental and improves the yield of polymerizable monomer, while the reduced steric encumbrance around the olefins results in enhanced polymerization rates due to the reduction in the number of coordinating side-chains.



Scheme 7. Initiation of Grubbs' second generation catalyst during ROMP of dialkoxy-substituted [2.2]paracyclophane-1,9-diene. L = PCy_3, R = alkyl. Reproduced from Ref. 82 with permission from the Royal Society of Chemistry.

Turner and coworkers studied the reactivity of the diethylhexyloxy-pCpd that forms **P4** with GII and found the reactivity to be consistent with the catalyst coordinating to either face of the pCpd olefin. As there is not significant polarization to the olefin, there is no electronic effect that biases how the pCpd monomer opens (unlike for the BTD-pCpd, see section 4).[65] Dialkoxy-pCpds can open with either the *para*-alkoxy-substituted benzene ring or the unsubstituted benzene ring closer to the ruthenium catalyst depending on how the monomer was approached manifesting in lower regioregularity.[83] When the stabilizing alkoxy-benzene is closer to the catalyst, it can either displace the ancillary phosphine ligand and coordinate to the ruthenium to stabilize the catalyst, as with the tetraalkoxy-pCpds, or the ligand can re-coordinate (**Scheme 7**).[82] Additionally, when the unsubstituted benzene is closer to the Ru, the catalyst is more reactive, enabling shorter reactions times, because re-initiation of the catalyst is not required with every addition of monomer.

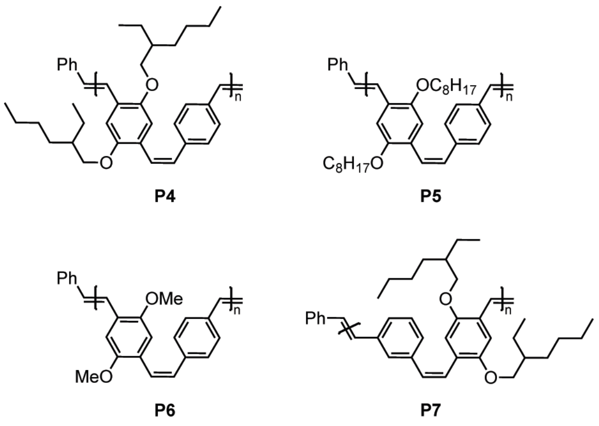
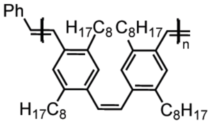


Figure 3. PPVs synthesized from dialkoxy-substituted [2.2]paracyclophane-1,9-diene and [2.2]metaparacyclophane-1,9-diene.

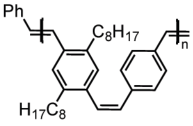
To date, four *para*-alkoxy-cyclophanedienes have been reported that afford PPVs. The first was reported by Turner and coworkers in 2010 and contained 2-ethylhexyloxy side-chains, a branched alkane that breaks up polymer aggregation, to afford **P4**.[44] The other two *para*-PPVs synthesized from dialkoxy-pCpds contain *n*-octyloxy moieties or methoxy groups to afford **P5** and **P6** respectively (**Figure 3**).[84-85] Incorporation of the *para*-(*2*-ethylhexlyoxy)-benzene with a bridged *meta*-benzene has also been synthesized and ring-opened to afford poly(*m*-phenylenevinylene-*co*-2,5-diethylhexyloxy-*p*-phenylenevinylene) (**P7**).[44, 86] While the *meta*-*para*-pCpd has a ring strain energy 7.6 kcal•mol^{-1} less than that of pCpd (**Figure 2**), **P7** is reported with a similar narrow dispersity compared to its all-*para* counterpart **P4** indicating it is a good, highly strained monomer for ROMP (**Table 1**). The optical properties of those PPVs, if reported, are described in Table 1. Notably, the *meta*-*para*-PPV, **P7**, is blue-shifted about 30 nm compared to its all-*para* counterpart **P4** showing the effects of substitution in the backbone on the optical properties of PPV.

3.3 ROMP of Tetraalkyl and Dialkyl [2.2]Paracyclophane-1,9-diene

While alkoxy side-chains on PPVs are better for ensuring their solubility, the electron-donating groups increase the electron density on the conjugated backbone which alters its bandgap and shifts the optical properties of the polymers: red-shifted for *para*-alkoxybenzene-PPVs and blue-shifted for *ortho*-alkoxybenzene-PPVs compared to unsubstituted PPV.[11] Inclusion of alkyl side-chains, which are weaker doners than alkoxy groups, maintain very similar optical properties to unsubstituted PPV while having significantly improved solubility.[87]



P8



P9

Figure 4. PPVs synthesized from alkyl-substituted [2.2]paracyclophane-1,9-diene.

The Turner group investigated the synthesis and ROMP of *n*-octyl containing tetraalkyl-pCpd and dialkyl-pCpd.[43] Both alkyl-containing pCpds polymerized in a controlled fashion to afford polymers with narrow dispersities. Just as with the tetraalkoxy-pCpd, only the pseudo-geminal isomer of the tetraalkyl could be ring-opened to afford PPV **P8** (**Figure 4**). Additionally, as these pCpds do not contain any moieties that can coordinate to the ruthenium catalyst, the ROMP of alkyl-pCpds can be achieved with shorter reactions times and at lower temperatures.[79]

3.4 ROMP of Substituted [2.2.2]Paracyclophane-1,9,17-triene

With the success of obtaining PPVs with narrow dispersities from a variety of pCpd monomers, larger cyclophane compounds that are more easily afforded have been identified for synthesizing PPVs to access more diverse substitution patterns. Bunz and coworkers synthesized dialkyl, dialkoxy, and tetraalkoxy-substituted pCpts to afford a library of unique PPVs (**Figure 5**). Just as with the tetrasubstituted pCpds, the tetrasubstituted pCpts form two diastereomers, the *cisoid* and the *transoid* conformation of the aryl rings; both pCpt diasteromers, however, are reactive with olefin metathesis catalysts.[64] Using GIII or HGII, the pCpts could be ring-opened and, like the previously examined pCpd monomers, there are no electronic effects that biases the regioselectivity of the pCpt monomers opening. The one alkyl-substituted triene containing *n*-dodecyl side-chains was reacted with the ruthenium catalyst in refluxing tetrahydrofuran (boiling point of 66 ˚C) while all alkoxy-substituted trienes required ROMP in refluxing toluene (boiling point of 110 ˚C) due to the coordination of the aryl ether oxygen as an anchoring group to the catalyst.[63-64] Higher temperatures are required and higher dispersities are reported for PPVs synthesized from pCpt, however, compared to that of pCpd. For example, comparing the ROMP of pCpt and pCpd each bearing four alkoxy side-chains, the pCpd monomers are polymerized around 55 ˚C with dispersities between 1.19-1.3 while the pCpt monomers required refluxing toluene with a reported dispersity of 1.9 for both (**Table 1**).[42, 64] These higher temperatures and dispersities can be attributed to the significantly lower ring strain of pCpt (13.1 kcal•mol^{-1}) compared to that of pCpd (39.4 kcal•mol^{-1}) resulting in a decreased living character of the polymerization (**Figure 2**).

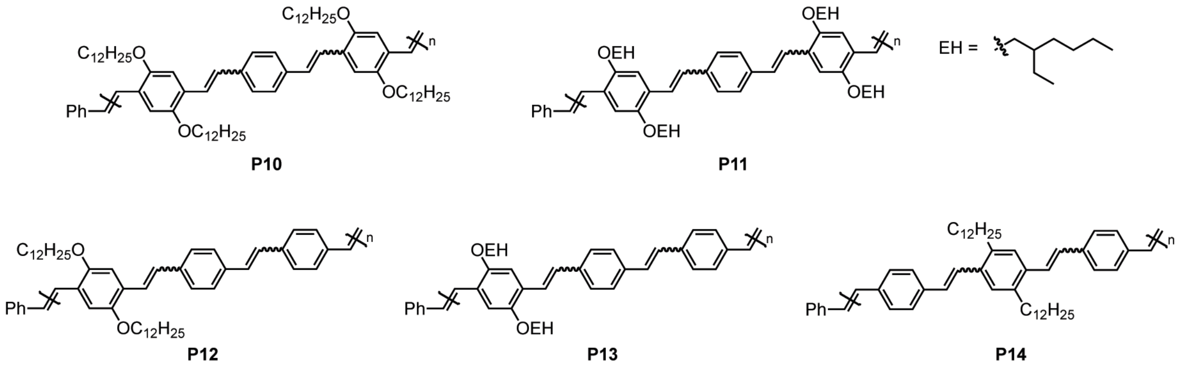


Figure 5. PPVs synthesized from alkyl and alkoxy-substituted [2.2.2]paracyclophane-1,9,17-diene. EH = 2-ethylhexyl

4. Ring-Opening Metathesis Polymerization of Cyclophanes to Afford Poly(arylene vinylene)s

As described in the introduction, the current use of PPVs as conducting/semiconducting materials is limited. Instead, organic photovoltaic materials are now dominated by donor-acceptor materials that enables engineering of their bandgap.[3, 14] Synthesis of donor-acceptor polymers, however, are typically accomplished by poorly-controlled cross-coupling/polycondensation methods (or the use of iterative synthetic techniques) that do not lend themselves to the formation of high-molecular weight polymers.[34-35, 88] Recent advances have been made toward living chain-growth polymerization for donor-acceptor polymers with the newly reported BTD-pCpd. Incorporating 2,1,3-benzothiadiazole (an acceptor motif) with a substituted phenyl moiety (a donor motif) into a cyclophanediene enables living ROMP to access a donor-acceptor poly(*p*-phenylene-*co*-arylene vinylene). It should be noted that other larger donor and acceptor aryl-cyclophanes have been assembled and ring-opened to afford poly(arylene vinylene)s that are more commonly synthesized by ADMET (not a living polymerization)[34-35] but, similarly to the previously examined pCpt, these larger cyclophanes contain less ring strain and result in polymers with higher dispersities.[89-93] Additionally, these cyclophane monomers are out of the scope of this review as they do not contain an alkylphenylene or alkoxyphenylene units.

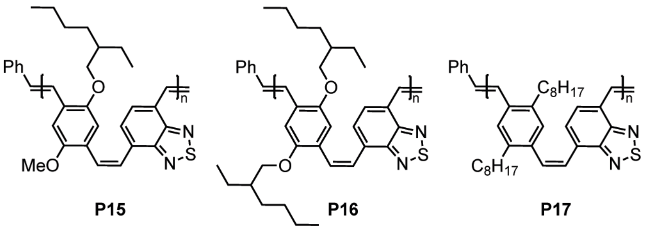


Figure 6. Poly(*p*-phenylene-*co*-benzothiadiazole vinylene)s synthesized from alkyl and alkoxy-substituted benzothiadiazole-[2.2]paracyclophane-1,9-diene.

The groups of Elacqua and Turner independently reported the synthesis and use of BTD-pCpd as a new class of cyclophane monomers. Elacqua reported MEH-PPV-*co*-BTD **P15** and established the living nature of the ROMP of BTD-pCpd using GII or HGII,[65] likely enabled by the high strain energy of the diene (36.5 kcal•mol^{-1} according to our DFT calculations). The Turner group expanded the scope by reporting both alkoxy and alkyl polymers **P16** and **P17** respectively (**Figure 6**). Additionally, Turner described the photoisomerization of these poly(arylene vinylene) from the *cis,trans* conformation to the all-*trans* polymer.[66] The properties of all the poly(*p*-phenylene-*co*-benzothiadiazole vinylene)s homoblocks are reported in **Table 2**.

Cyclophane	Polymer	DP	Đ	λ abs. max. (nm) solution[a)]	λ em. max. (nm) solution	Reference
BTD-[2.2]paracyclophane-1,9-diene	**P15**	15	1.27	555	682, 710 (sh)	[65]
	P16	20	1.3	505	637	[66]
	P17	20	1.5	469	596	[66]

Table 2. Summary of the optical properties of PPVs synthesized by ROMP of benzothiadiazole-[2.2]paracyclophane-1,9-diene. a)absorbance reported of the *cis,trans* polymer prior to photoisomerization. BTD = 2,1,3-Benzothiadiazole

The ROMP of BTD-pCpd is believed to afford well-defined alternating donor-acceptor conjugated polymers due to the polarization of the olefins. The initiation of the monomer was observed to be non-regiospecific as coordination of the aryl ether and the nitrogen of the benzothiadiazole to the ruthenium carbene was observed by *in situ* ^{1}H NMR kinetic experiments.[66] It is thought that the propagation steps of the polymerization are regiospecific to give alternating donor-acceptor polymers as the presence of significant sequences of donor-donor diads or acceptor-acceptor diads are not observed.[66]

5. Ruthenium Catalysts

For the ROMP of cyclophane monomers, the choice of catalyst is of paramount importance for the polymer's structural conformation and properties. In previous sections, only linear polymers were examined that were polymerized (in a living chain-growth manner) with GII,[94] the fast initiating GIII,[95] or HGII (**Figure 7**).[96] These are not the only catalysts that can be used to initiate ROMP. Instead using strategically designed olefin metathesis catalysts, different end-group functionality, polymer stereochemistry, and polymer architectures can be achieved. This section will detail, chronologically, the use of ruthenium catalysts beyond GII, GIII, and HGIII for the ring-opening of substituted pCpds and the polymers that result.

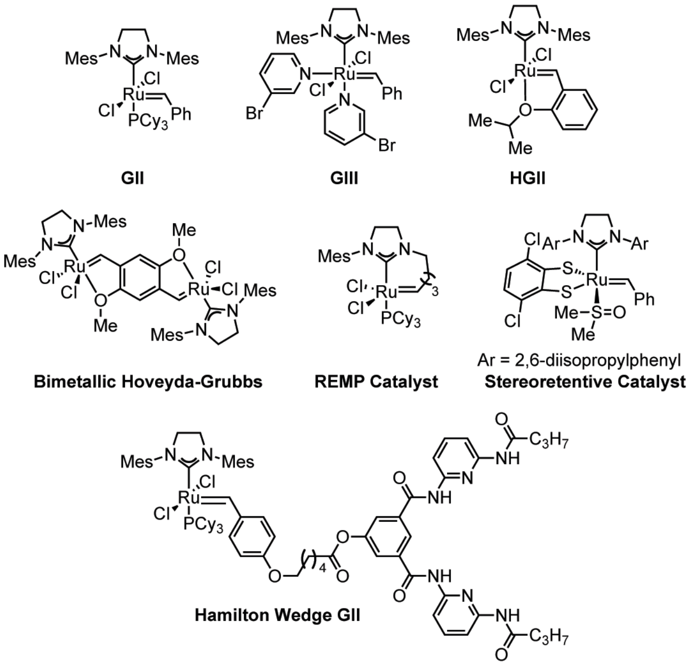


Figure 7. Ruthenium catalysts used for the polymerization of cyclophane monomers. REMP = ring-expansion metathesis polymerization

5.1 Functionalized Ruthenium Initiator

The mechanism for the initiation of ROMP requires a formal [2+2] cycloaddition between the olefin and the ruthenium catalyst, followed by the incorporation of an alkylidene at the initiating end of the polymer after the metallacyclobutane cyclo-reversion. For GII and GIII this alkylidene results in a styrene unit at the initiating end while for HGII the alkylidene results in the incorporation of a 2-isopropoxystyrene moiety.[97] Many groups have shown that different functional groups can be incorporated into olefin metathesis catalysts using alkylidene exchange reactions with Grubbs catalysts to afford heterotelechelic polymers.[98-100] Our group has used this strategy to prepare many functionalized Grubbs initiators with molecular recognition units that allow for the supramolecular assembly of block copolymers.[101-102] For the use with cyclophanes specifically, we prepared an *N*,*N*′-bis[6-(alkanoylamino)pyridin-2-yl]isophthalamide (commonly referred to as the Hamilton wedge)[103] functionalized GII catalyst (Figure 7). Using this **Hamilton Wedge GII** initiator, dioctyloxy-[2.2]pCpd was polymerized to afford a Hamilton wedge-dioctyloxy-PPV that is capable of forming supramolecular assemblies with the complementary barbiturate unit.[84] The applications of PPVs in supramolecular assemblies using this catalyst will be further examined in section 6.3.

5.2 Ring-Expansion Metathesis Polymerization (REMP) Catalyst

Macrocyclic conjugated polymers have also been explored and are of interest because of their distinct optoelectronic properties compared to their linear analogues. The macrocycles band gap can be easily tuned with the incorporation of different amounts of phenylene units.[104] As a result, macrocyclic conjugated systems can outperform their linear analogues as the active component in organic electronics.[105] While many conjugated macrocycles have been reported, such as cycloparaphenylenes (commonly referred to as carbon nanohoops),[106] the incorporation of olefin subunits into conjugated macrocycles is uncommon. Investigating cyclic PPVs could lead to different optoelectronic properties than their linear counterparts, causing altered conjugation length and enhanced sensitive to their environment.[107-109]

The Turner group has bridged the gap toward synthesizing macrocyclic PPVs by using substituted pCpd monomers to perform ring-expansion metathesis polymerization (REMP). Using the **REMP Catalyst** (Figure 7) where the *N*-heterocyclic carbene is tethered to the alkylidene unit on the ruthenium,[110] dioctyl-pCpd and diethylhexyloxy-pCpd were investigated for REMP. The alkyl-pCpd efficiently led to cyclic polymers, while the REMP of the alkoxy-pCpd was deactivated by the coordination of the alkoxy side-chain to the catalyst. Successful REMP of the dioctyl-pCpd formed three major cyclic *cis,trans*-PPVs composed of six or seven repeat units, indicating that there is no control of the regiochemistry during the secondary metathesis that leads to ring extrusion. Using single-molecule spectroscopy, the cyclic PPVs were found to adopt a restricted ring-like conformation that results in shorter conjugation lengths compared to that of their linear counterparts. As a result, the linear and the cyclic PPVs have surprisingly similar spectral properties.[111] With new REMP catalysts being reported,[112-113] an apparent resurgence of REMP is underway and one can expect more cyclic PPVs to be synthesized incorporating different ring sizes that could result in different optical properties.

5.3 Bidirectional ROMP

Using conventional Grubbs or Hoveyda-Grubbs initiators for ROMP results in polymers synthesized with unidirectional growth with a clear initiating end and terminus. Using bimetallic complexes, however, allow for a bidirectional polymerization because both metals can undergo ROMP independently. Barbasiewicz and coworkers reported the **Bimetallic Hoveyda-Grubbs** catalyst by reacting GII with 1,4-dimethoxy-2,5-divinylbenzene (Figure 7).[114] The Turner group used this catalyst with their alkyl and alkoxy-substituted pCpds, and found that it enables living ROMP. Using this strategy affords symmetric tri- and penta-block copolymers via block extension.[115] Homotelechelic PPVs are also accessible with this strategy when the ROMP is terminated with a functional moiety.[116] This is distinct to monodirectional ROMP catalysts, such as with GII, in which homotelechelic PPVs are difficult to access due to the incorporation of the benzylidene upon initiation and other functional groups upon termination with vinyl ethers. The Turner group, as a proof-of-concept, showed that by terminating the polymerization with an α-bromoester phenyl methylvinyl ether (an ATRP initiator) they could initiate further polymerization to afford a coil-rod-coil block copolymer.[115]

5.4 All-*cis*-PPV

All-*trans*-PPV perform better in devices due to their rodlike structure which increases π-π interactions during packing, enabling inter-chain transfer of electrons and holes.[11, 117] *cis*-Rich PPVs instead adopt a twisted polymer chain structure that results in an overall decreased conjugation length but a more soluble polymer. The solubility of *cis*-rich PPVs can be leveraged during the synthesis and fabrication steps, given that *cis*-vinyl-linkages are easily fully photoisomerized to their corresponding *trans*-PPV in both solution and the solid state.[118] Using the previously discussed catalysts for the living ROMP of substituted pCpds, however, affords the *cis,trans*-PPV exclusively. All-*cis*-PPVs have been afforded previously by Katayama and Ozawa using Suzuki-Miyaura polymerizations[118-119] or by the Swager group using post-polymerization reduction of poly(phenylene ethynylene)s.[120] These strategies for accessing all-*cis*-PPVs are based on uncontrolled chain-growth polymerizations yielding disperse PPVs with no control over molecular weight or end-groups.

Z-selective ruthenium catalysts have recently been reported for the retention of alkene stereochemistry during metathesis for various monomers.[121-126] Michaudel and coworkers recently reported the stereoretentive ROMP of substituted pCpds using the dithiolate-chelated **Stereoretentive Catalyst** (Figure 7). Initial studies with dioctyloxy-pCpd proved the stereoretentive ROMP, when performed in the dark, affords all-*cis*-**P5** with perfect stereoselectivity, narrow dispersities, and controlled average molar masses based off the monomer-to-catalyst feed-ratio.[127] They further examined the stereoretentive ROMP to afford polymers **P4** and **P9** which were both living. Remarkably, using the diethylhexyloxy-pCpd to decrease aggregation of the conjugated polymer, they reported **P4** with a remarkably high degree of polymerization (X = 236), the highest reported degree of polymerization for a soluble PPV.[128] As such, the choice of catalyst is a powerful tool for modulating the properties of PPVs, and can dramatically affect the potential applications of such polymers.

6. Block Copolymers

6.1 Conjugated Block Copolymers

Due to the living nature of ROMP, different cyclophanes can be polymerized to afford PPV block copolymers which have optoelectronic properties distinct from PPV homopolymers. Turner and coworkers have examined the combinations of alkyl-pCpds, alkoxy-pCpds, alkoxy-meta-pCpd, and BTD-pCpd (with alkyl or alkoxy side-chains) to afford multiblock copolymers via living ROMP.[44, 86, 115, 129] Yu *et al.* reported a PPV-naphthylenevinylene block copolymer with tetraalkoxy-pCpds using the same strategy.[130] The potential for easily accessing conjugated block copolymers via ROMP is advantageous for optoelectronic purposes but will not be further examined in this review. Instead, this section will focus on the diversity of PPV block copolymers obtained via ROMP of substituted pCpds.

6.2 Partially Conjugated Block Copolymers

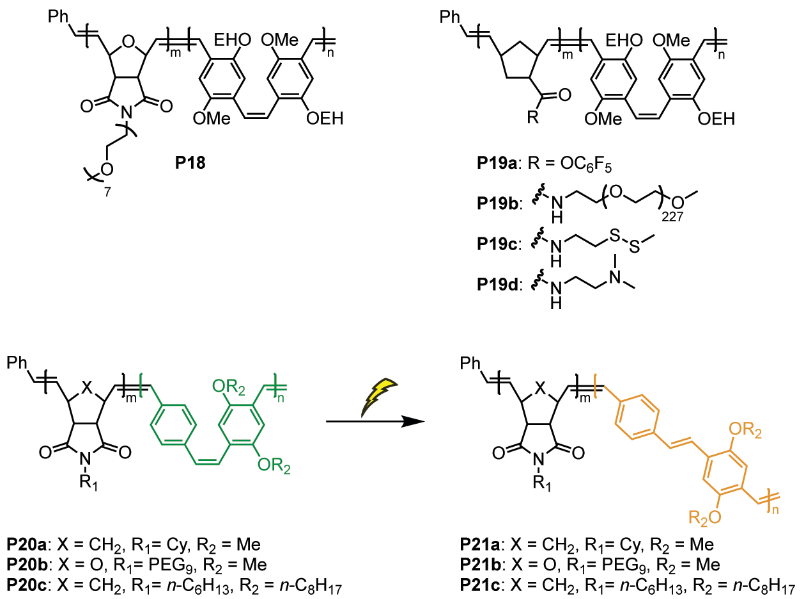


Figure 8. Partially conjugated block copolymers synthesized with alkoxy-substituted [2.2]paracyclophane-1,9-diene. EH = 2-ethylhexyl

Combining strategies for the ROMP of aliphatic olefins with the ROMP of substituted pCpds results in polymers containing a conjugated block and a non-conjugated block. These copolymers containing different blocks are useful for material science, as amphiphilic block copolymers can arrange into various nanostructures, resulting potentially in varied conductivity and tunable optoelectronic properties.[131-133] Additionally, amphiphilic polymers have been used in applications such as drug delivery[134-135] and as catalytic nanoreactors.[136-138] PPV-containing amphiphilic diblock copolymers have previously been reported in literature, synthesized by non-living methods, and the PPV blocks exhibited liquid crystallinity with electrical and optical properties.[139-140] Two main strategies for the assembly of block copolymers using ROMP with substituted pCpds and a second non-conjugated monomer are: to polymerize pCpd blocks via ROMP followed by the addition of an aliphatic cyclic olefins to enchain monomers other than pCpd before termination. The other is to terminate the ROMP of pCpds with the initiator for another type of polymerization. The Turner group has reported the latter strategy by terminating the ROMP with an ATRP initiator,[115-116] while our group has reported an ethynyl palladium (II) chain-terminating agent that initiates the coordination/insertion polymerization of isocyanides.[141-142] The former chain-extension strategy presented, however, has primarily been investigated, with the comonomer most commonly used being norbornenes and oxanorbornenes.

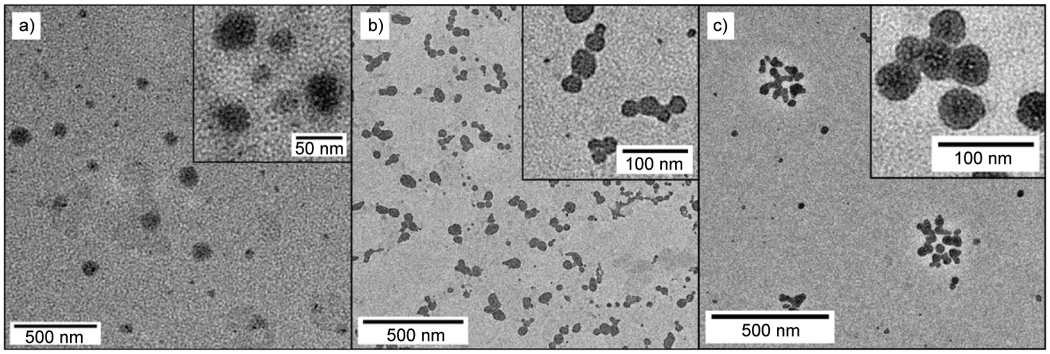


Figure 9. TEM images of self-assembled amphiphilic polymer **P19b** obtained using different protocols. a) micelles, b) partially fused micelles in the shape of caterpillars, and c) merging of micelles leading to larger aggregates. Reprinted with permission from ref. 143. Copyright 2016, American Chemical Society.

Choi, Zentel, and coworkers synthesized low dispersity diblock copolymers **P18** and **P19b** with different block ratios containing a block of MEH-PPV **P2** (kept in the dark to maintain its *cis, trans* microstructure) with either poly(norbornene) or poly(oxanorbornene) blocks containing poly(ethylene glycol) (PEG) side-chains. Their initial investigation of the self-assembly of the amphiphilic polymer using transmission electron microscopy (TEM) found that nanoparticles formed ranging in size from 60-95 nm.[143] The polymers formed micelles, spheres, caterpillar-like aggregates, or larger aggregates depending on how they were assembled (**Figure 9**). Each morphology results in distinct optical properties due to the aggregation and interchain chromophore order. The correlation of the aggregation state with electronic properties is very promising for the use of PPV-amphiphilic block copolymers synthesized by ROMP as their size, shape, and absorption properties can be fine-tuned for specific applications.

Quantum dots were also explored by Zentel and coworkers using **P19** containing the *cis,trans*-MEH-PPV **P2** block.[143] Beginning with **P19a** containing the electronically activated pentafluorobenzene ester, anchoring groups were appending by the formation of the amide as a post-polymerization modification bearing either a disulfide moiety (**P19c**) or a tertiary amine (**P19d**). Nanocomposites were prepared by reacting the polymer with CdSe/CdZnS core-shell quantum dots (enabled by the presence of the anchoring disulfide or amine groups). Using time-resolved photoluminescence measurements, a reduced lifetime of the quantum dots emission was observed signifying that there are interactions between the PPV-block copolymer and the quantum dots. This ability to use interactions between a conjugated block copolymer and quantum dots to tune photophysical properties is advantageous for applications in optoelectronic devices.

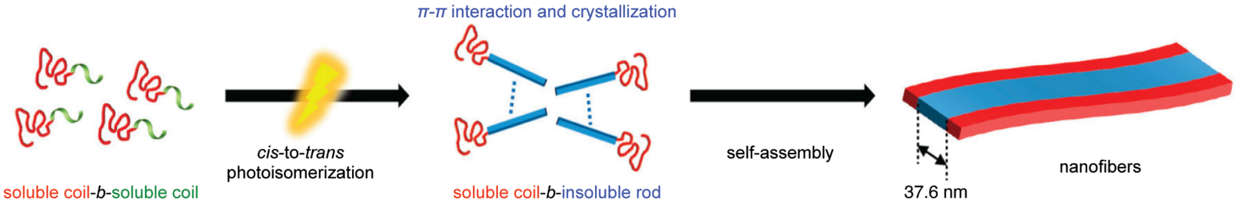


Figure 10. Schematic representation of the formation of nanofibers using light-induced crystallization-driven self-assembly. Reprinted with permission from ref. 85. Copyright 2018, American Chemical Society.

Utilizing the *cis,trans* or all-*cis* configuration of the olefins provided by ROMP, easily synthesized phototriggerable materials are an additional emerging application for amphiphilic PPV-diblock copolymers synthesized by ROMP of pCpds.[127] Similar to Katayama and Ozawa who have already shown that all-*cis*-PPV can be photopatterned,[118] Choi and coworkers have reported photoresponsive materials by what they term “one-shot ROMP”. Synthesizing diblock copolymers **P20a** and **P20b** in the dark (to avoid photoisomerization) they showed how the *cis,trans*-PPV materials are phototriggered to **P21a** and **P21b** respectively (**Figure 8**). Given the lower solubility of *trans*-rich PPVs, **P21a** and **P21b** undergo light-induced crystallization-driven self-assembly, causing the rapid assembly of nanofibers (**Figure 10**). The length of these nanofibers is easily controlled as their seeded growth is photoactivated and can be started or halted by turning the light on or off, demonstrating that these are responsive conjugated materials with precise control of their nanostructures. More advanced morphologies are also achievable using this seeded growth strategy to afford ABA triblock comicelles and gradient comicelles.[85]

Additionally, Michaudel and coworkers photoisomerized their all-*cis* block copolymer **P20c** to the all-*trans* **P21c**, noting larger hydrodynamic radii consistent with a coil-to-rod transition of the conjugated system as well as a concomitant decrease in solubility in THF.[127] This strategy for responsive conjugated materials using light (an easily controlled spatiotemporal stimulus) allows for the precise control of nanostructures which can be designed for various applications.

Other amphiphilic block copolymers for soft materials have been synthesized by Choi and coworkers for soft materials using unsubstituted-pCpd monomers.[144-145] These examples showed the formation of unique fractal nanostructures and the ability of PPV-containing nanoparticles to be used chemical sensors. Both applications should also be applicable to their more soluble substituted-PPV derivatives, but are yet to be reported.

6.3 Supramolecular Block Copolymers

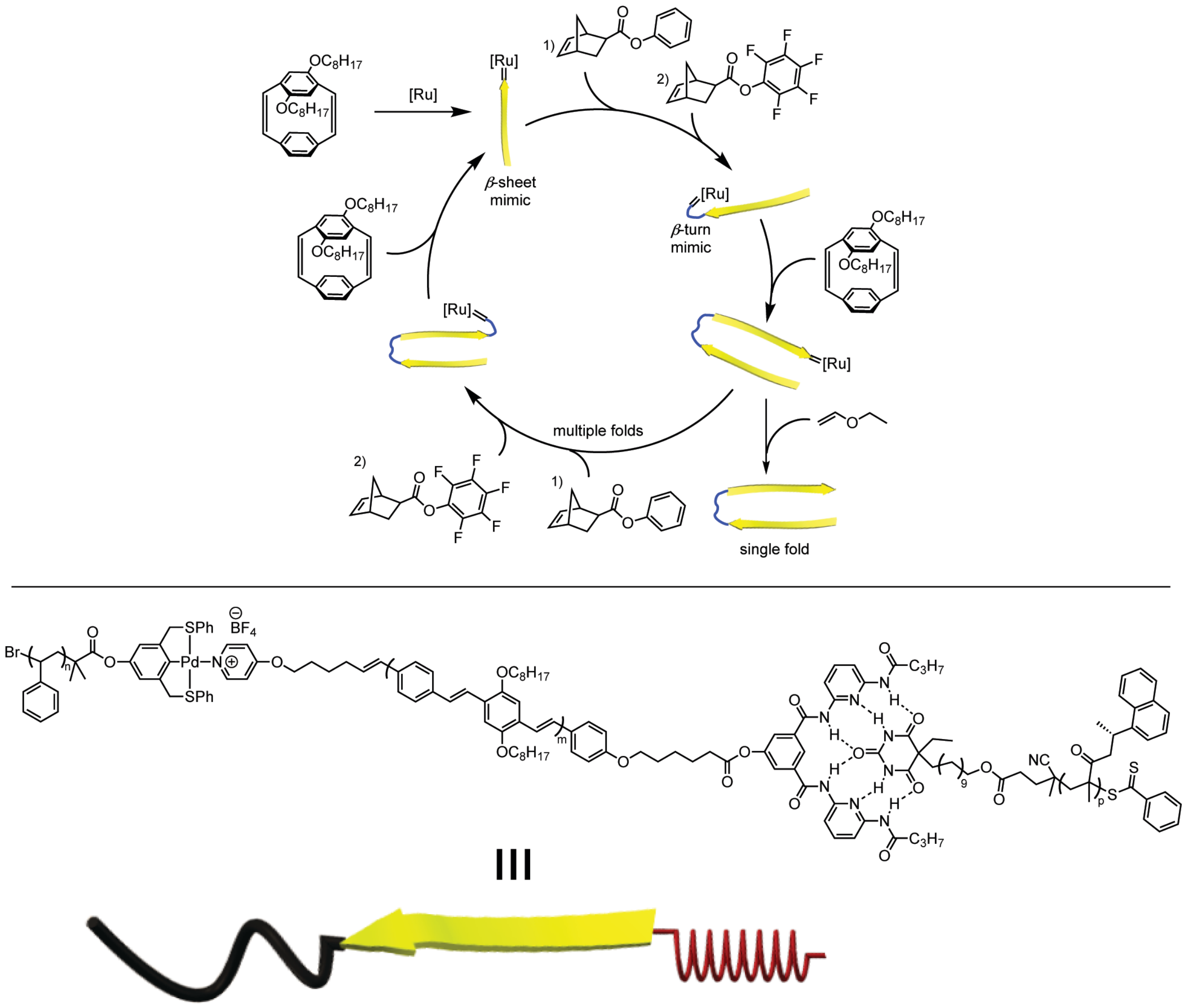


Figure 11. PPV β-sheet mimics for protein architecture mimics in supramolecular polymers. (Top) Catalytic cycle for the formation of β-sheet like structures synthesized by the ring-opening metathesis polymerization of [2.2]paracyclophane-1,9-diene. (Bottom) Schematic representation of a supramoleculary assembled non-peptidic based polymer containing secondary structure.

Biomacromolecules use supramolecular interaction that endow them specific functionality.[146] As such, many supramolecular polymer chemists aim to mimic the control of both covalent and noncovalent interactions exhibited in biomacromolecules to impart functionality to synthetic polymers. Our group specializes in the supramolecular assembly of polymers using orthogonal molecular recognition units (MRUs) that are dependent on hydrogen bonding, metal coordination, π-stacking, or host/guest interactions.[147-148] Our recent work has been focused on mimicking protein architectures and achieving local tertiary structures by combining nonpeptidic block copolymers that have a predefined secondary structure (**Figure 11**).[149-150] For α-helix mimics, we use poly(methacrylamide)s (PMAcs) and/or poly(isocyanide)s (PICs) and for random coils we have prepared poly(styrene)s or poly(norbornene)s. Our β-sheet mimics are PPVs synthesized via ROMP of either tetraoctyloxy-pCpd or dioctyloxy-pCpd to form **P1** or **P5** respectively.

The properties of PPVs make them close mimics of β-sheet for non-amide-based polymers due to their face-to-face π-stacking or interdigitation of their alkyl side-chains, which mimics the interactions in β-sheets. By strategically planning our fabrication process of these π-sheets, we can afford sheets that are telechelic, homotelechelic, or heterotelechelic by taking advantage of functionalized ruthenium initiators (such as the **Hamilton Wedge GII** discussed in section 5.1) and functionalized terminating agents to install MRUs at the sheet's head and tail. Using our strategy, a single stranded sheet is easily synthesized in addition to both parallel and anti-parallel β-sheet-like structures. Parallel π-sheets are assembled by the supramolecular assembly of two π-sheets.[84, 151] The anti-parallel π-sheets, however, are synthesized as a multiblock copolymer. Taking advantage of the living polymerization, blocks of PPV are incorporated between short sections of poly(norbornene)s with benzene and pentafluorobenzene moieties. Due to the interactions between phenyl and pentafluorophenyl groups, these polynorbornene sections fold, behaving as a β-hairpin turn to fold the sheets into place (Figure 11 top).[84, 152] Using single-molecule polarization studies, we have confirmed that our β-sheet mimics fold effectively.[153]

In 2015, we demonstrated that two blocks of PPVs can be supramolecularly assembled by hydrogen bonding or metal coordination when their polymerization is terminated with the appropriate vinyl ether-based MRUs.[151] This strategy was expanded to make supramolecular PPV diblock copolymers composed of different secondary structures with homotelechelic PMAc, PIC, and poly(norbornene) bearing the complementary MRU to make what we see as sheet-helix and sheet-coil protein architecture mimics.[84] Our most advanced systems at mimicking a local tertiary structure of proteins uses a heterotelechelic PPV synthesized with the **Hamilton Wedge GII** initiator and terminated with a pyridine functionalized chain terminating agent. This Hamilton wedge-PPV-Pyridine block was then assembled with a helical PMAc polymer terminated with the SCS-Pincer-Pd^{II} (metal coordination MRU with the pyridine) and a barbiturate-containing styrene block to orthogonally assemble into a coil-sheet-helix structure (Figure 11 bottom).[84] Our protein mimetic polymers would not have been possible without the control imparted by ROMP for the synthesis of narrowly disperse PPV polymers with control over the molecular weight, sequence, and end-groups. We envision that as strategies enabling precise control over polymer synthesis (such as the living ROMP of pCpds) become more established, greater functionality and control over polymer architecture will be achieved, enabling the next generation of functional materials.

7. Conclusion

The use of substituted cyclophane monomers for ring-opening metathesis polymerization to access poly(*p*-phenyene vinylenes) and poly(*p*-phenylene-*co*-arylene vinylene)s is a powerful tool, enabling controlled polymerization, tunable molecular weights, low dispersities and the potential for block copolymer formation. Examining tetrasubstituted and disubstituted alkyl and alkoxy [2.2]paracyclophane-1,9-diene, [2.2]metaparacyclophane-1,9-diene, [2.2.2]paracyclophane-1,9,17-triene, and BTD-[2.2]paracyclophane-1,9-diene, it appears that the smaller cyclophane systems with greater ring strain are better monomers for synthesizing narrowly disperse conjugated vinylene polymers. Alkoxy-substituted pCpd monomers are the most beneficial to the polymerization for two reasons: (1) the aryl-ether oxygen coordinates to the ruthenium catalyst, stabilizing the catalyst and providing a more-controlled polymerization and (2) they endow the PPV with alkoxy side-chains which is highly beneficial for the polymers solubility. Taking advantage of ROMP, the afforded polymers can be strategically designed to incorporate the same or different functional groups at the termini and they can be synthesized into block copolymers allowing for various applications such as optoelectronic materials, photoresponsive materials, and controlled polymeric architectures.

Despite the monomers and polymers reviewed herein, the ROMP of cyclophanes is still in its infancy, given the limited number of functionalized cyclophanes that can be achieved resulting in soluble polymers. We envision future opportunities in this area are related to expanding this currently small library specifically of pCpd monomers. We expect greater structural diversity in pCpd monomers will enable access to more functional PPVs by enabling the incorporation of reactive side-chains and side-chains that can modulate the properties of the resulting polymers. One potential way for accessing greater diversity in pCpds is by adapting more palladium cross-coupling reactions on cyclophanedienes.[59] We expect more hydrophilic side-chains will enable water-solubility, which could be ideal for biological sensing purposes where PPVs are mainly being explored at the moment.[20] Additionally, incorporating enantiomerically pure side-chains can impact the PPVs stacking behavior and thus its fluorescence.[154] Another way to diversify pCpd monomers is to introduce other aromatic moieties into the pCpd core (similar to previous efforts incorporating 2,1,3-benzothiadiazole) enabling new donor-acceptor copolymers with distinct optoelectronic properties compared to that of PPV homopolymers. According to MacDiarmid, we live in a materials-limited world,[3] and as such, a very promising future awaits as pCpd and PPV materials continue to be developed with novel functionality and applications.

Acknowledgements

The authors acknowledge financial support from the National Science Foundation under award number CHE 2203929. The authors thank the NYU IT High Performance Computing center for resources, services, and staff expertise. Arielle Mann thanks the NYU Department of Chemistry for support in the form of a Margaret Strauss Kramer Fellowship. We thank Stephen J. Koehler for providing thoughtful comments.

Biographies

Arielle Mann received her B.S. in chemistry from Tufts University in 2018. While there she worked on mechanofluorochromic materials under Samuel W. Thomas III. Currently, she is a Ph.D. candidate in the laboratory of Marcus Weck at New York University. Her research focuses on the development of new cyclophanediene monomers for β-sheet-mimicking polymers.

Matthew D. Hannigan obtained his Ph.D. in Chemistry in 2022 from the University of Michigan, working with Professors Anne J. McNeil and Paul M. Zimmerman. He is currently a postdoctoral associate in Prof. Marcus Weck's lab at New York University. His research interests include organometallic polymerizations, living polymerizations, and the synthesis of polymers with well-defined secondary structure.

Marcus Weck obtained his Ph.D. degree in 1998 from Caltech with Robert H. Grubbs. After a postdoctoral stay at Harvard University with George M. Whitesides, he joined the faculty at Georgia Tech. In 2007, he moved to New York University, where he is a professor in the chemistry department. His research interests are in organic and polymer chemistry as well as materials science. The main foci of his group are supported catalysis, the introduction of complexity through the use of orthogonal functionalization methods, and to synthesize polymers, organized assemblies, biomaterials, and nanostructures.

References:

[1] C. K. Chiang, C. R. Fincher, Y. W. Park, A. J. Heeger, H. Shirakawa, E. J. Louis, S. C. Gau, A. G. MacDiarmid, *Phys. Rev. Lett.* **1977**, *39*, 1098.

[2] A. J. Heeger, *Angew. Chem. Int. Ed.* **2001**, *40*, 2591.

[3] T. M. Swager, *Macromolecules* **2017**, *50*, 4867.

[4] A. Kraft, A. C. Grimsdale, A. B. Holmes, *Angew. Chem. Int. Ed.* **1998**, *37*, 402.

[5] J. H. Burroughes, D. D. C. Bradley, A. R. Brown, R. N. Marks, K. Mackay, R. H. Friend, P. L. Burns, A. B. Holmes, *Nature* **1990**, *347*, 539.

[6] M. Kuik, G.-J. A. H. Wetzelaer, H. T. Nicolai, N. I. Craciun, D. M. De Leeuw, P. W. M. Blom, *Adv. Mater.* **2014**, *26*, 512.

[7] A. Greiner, *Polym. Adv. Technol.* **1998**, *9*, 371.

[8] U. Mitschke, P. Bäuerle, *J. Mater. Chem.* **2000**, *10*, 1471.

[9] M. T. Bernius, M. Inbasekaran, J. O'Brien, W. Wu, *Adv. Mater.* **2000**, *12*, 1737.

[10] F. Babudri, G. M. Farinola, F. Naso, R. Ragni, *Chem. Commun.* **2007**, 1003.

[11] A. C. Grimsdale, K. L. Chan, R. E. Martin, P. G. Jokisz, A. B. Holmes, *Chem. Rev.* **2009**, *109*, 897.

[12] S. W. Thomas, G. D. Joly, T. M. Swager, *Chem. Rev.* **2007**, *107*, 1339.

[13] A. J. Heeger, *Chem. Soc. Rev.* **2010**, *39*, 2354.

[14] R. M. Pankow, B. C. Thompson, *Polymer* **2020**, *207*, 122874.

[15] C. Wu, C. Szymanski, Z. Cain, J. McNeill, *J. Am. Chem. Soc.* **2007**, *129*, 12904.

[16] C. Wu, B. Bull, C. Szymanski, K. Christensen, J. McNeill, *ACS Nano* **2008**, *2*, 2415.

[17] S. Kim, C.-K. Lim, J. Na, Y.-D. Lee, K. Kim, K. Choi, J. F. Leary, I. C. Kwon, *Chem. Commun.* **2010**, *46*, 1617.

[18] M. Doshi, M. Krienke, S. Khederzadeh, H. Sanchez, A. Copik, J. Oyer, A. J. Gesquiere, *RSC Adv.* **2015**, *5*, 37943.

[19] Q. Miao, C. Xie, X. Zhen, Y. Lyu, H. Duan, X. Liu, J. V. Jokerst, K. Pu, *Nat. Biotechnol.* **2017**, *35*, 1102.

[20] Y. Chen, L. Zhou, J. Wang, X. Liu, H. Lu, L. Liu, F. Lv, S. Wang, *ACS Appl. Mater. Interfaces* **2018**, *10*, 27555.

[21] X. Zhen, C. Xie, K. Pu, *Angew. Chem. Int. Ed.* **2018**, *57*, 3938.

[22] Y. Lyu, D. Cui, J. Huang, W. Fan, Y. Miao, K. Pu, *Angew. Chem. Int. Ed.* **2019**, *58*, 4983.

[23] C. Ma, Z. Wang, X. Huang, G. Lu, I. Manners, M. A. Winnik, C. Feng, *Macromolecules* **2020**, *53*, 8009.

[24] C. Ma, D. Tao, Y. Cui, X. Huang, G. Lu, C. Feng, *Macromolecules* **2020**, *53*, 8631.

[25] H. Lin, H. Bai, Z. Yang, Q. Shen, M. Li, Y. Huang, F. Lv, S. Wang, *Chem. Commun.* **2022**, *58*, 7232.

[26] T. Junkers, J. Vandenbergh, P. Adriaensens, L. Lutsen, D. Vanderzande, *Polym. Chem.* **2012**, *3*, 275.

[27] T. Schwalm, J. Wiesecke, S. Immel, M. Rehahn, *Macromol. Rapid Commun.* **2009**, *30*, 1295.

[28] J. Freudenberg, D. Jänsch, F. Hinkel, U. H. F. Bunz, *Chem. Rev.* **2018**, *118*, 5598.

[29] A. J. Blayney, I. F. Perepichka, F. Wudl, D. F. Perepichka, *Isr. J. Chem.* **2014**, *54*, 674.

[30] M. Nojima, Y. Ohta, T. Yokozawa, *J. Polym. Sci. A Polym. Chem.* **2014**, *52*, 2643.

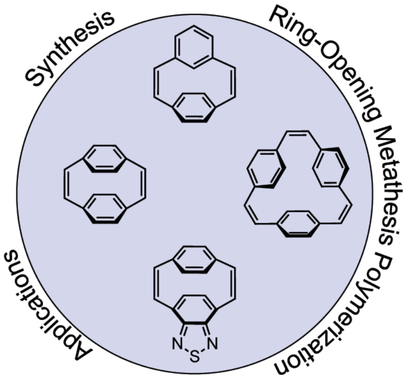
[31] M. Nojima, R. Saito, Y. Ohta, T. Yokozawa, *J. Polym. Sci. A Polym. Chem.* **2015**, *53*, 543.

[32] A. Menon, H. Dong, Z. I. Niazimbetova, L. J. Rothberg, M. E. Galvin, *Chem. Mater.* **2002**, *14*, 3668.
[33] N. Zaquen, L. Lutsen, D. Vanderzande, T. Junkers, *Polym. Chem.* **2016**, *7*, 1355.
[34] U. H. F. Bunz, D. Mäker, M. Porz, *Macromol Rapid Commun* **2012**, *33*, 886.
[35] Y. Chen, M. M. Abdellatif, K. Nomura, *Tetrahedron* **2018**, *74*, 619.
[36] V. P. Conticello, D. L. Gin, R. H. Grubbs, *J. Am. Chem. Soc.* **1992**, *114*, 9708.
[37] M. W. Wagaman, R. H. Grubbs, *Macromolecules* **1997**, *30*, 3978.
[38] Y.-J. Miao, G. C. Bazan, *J. Am. Chem. Soc.* **1994**, *116*, 9379.
[39] K. C. Dewhirst, D. J. Cram, *J. Am. Chem. Soc.* **1958**, *80*, 3115.
[40] R. H. Mitchell, V. Boekelheide, *J. Am. Chem. Soc.* **1974**, 1547.
[41] T. Otsubo, V. Boekelheide, *Tetrahedron Lett.* **1975**, *16*, 3881.
[42] C.-Y. Yu, M. Helliwell, J. Raftery, M. L. Turner, *Chem. Eur. J.* **2011**, *17*, 6991.
[43] B. J. Lidster, D. R. Kumar, A. M. Spring, C.-Y. Yu, M. Helliwell, J. Raftery, M. L. Turner, *Org. Biomol. Chem.* **2016**, *14*, 6079.
[44] C.-Y. Yu, M. Horie, A. M. Spring, K. Tremel, M. L. Turner, *Macromolecules* **2010**, *43*, 222.
[45] V. Boekelheide, P. H. Anderson, T. A. Hylton, *J. Am. Chem. Soc.* **1974**, *96*, 1558.
[46] M. Montanari, A. Bugana, A. K. Sharma, D. Pasini, *Org. Biomol. Chem.* **2011**, *9*, 5018.
[47] G. J. Bodwell, P. R. Nandaluru, *Isr. J. Chem.* **2012**, *52*, 105.
[48] M. Carnes, D. Buccella, J. Decatur, M. L. Steigerwald, C. Nuckolls, *Angew. Chem. Int. Ed.* **2008**, *47*, 2982.
[49] C. L. Coulter, K. N. Trueblood, *Acta Cryst.* **1963**, *16*, 667.
[50] D. E. Fagnani, A. Sotuyo, R. K. Castellano, *Comprehensive Supramolecular Chemistry II*, Elsevier, **2017**.
[51] S. Grimme, C. Mück-Lichtenfeld, *Isr. J. Chem.* **2012**, *52*, 180.
[52] D. J. Cram, J. M. Cram, *Acc. Chem. Res.* **1971**, *4*, 204.
[53] A. de Meijere, S. I. Kozhushkov, K. Rauch, H. Schill, S. P. Verevkin, M. Kümmerlin, H.-D. Beckhaus, C. Rüchardt, D. S. Yufit, *J. Am. Chem. Soc.* **2003**, *125*, 15110.
[54] Z. Hassan, E. Spuling, D. M. Knoll, S. Bräse, *Angew. Chem. Int. Ed.* **2020**, *59*, 2156.
[55] I. Erden, P. Gölitz, R. Näder, A. de Meijere, *Angew. Chem. Int. Ed.* **1981**, *20*, 583.
[56] M. Stöbbe, S. Kirchmeyer, G. Adiwidjaja, A. de Meijere, *Angew. Chem. Int. Ed.* **1986**, *25*, 171.
[57] M. Stöbbe, O. Reiser, T. Thiemann, R. G. Daniels, A. de Meijere, *Tetrahedron Lett.* **1986**, *27*, 2353.
[58] A. Mann, M. Weck, *ACS Macro Lett.* **2022**, *11*, 1055.
[59] C.-Y. Yu, Y.-C. Lai, *RSC Adv.* **2018**, *8*, 19341.
[60] C.-Y. Yu, Y.-C. Lai, *Macromol. Chem. Phys.* **2018**, *219*, 1800135.
[61] D. J. Cram, K. C. Dewhirst, *J. Am. Chem. Soc.* **1959**, *81*, 5963.
[62] D. Tanner, O. Wennerström, U. Norinder, K. Müllen, R. Trinks, *Tetrahedron* **1986**, *42*, 4499.
[63] D. Mäker, C. Maier, K. Brödner, U. H. F. Bunz, *ACS Macro Lett.* **2014**, *3*, 415.
[64] D. Mäker, U. H. F. Bunz, *Macromol. Rapid Commun.* **2014**, *35*, 2096.
[65] E. Elacqua, M. Gregor, *Angew. Chem. Int. Ed.* **2019**, *58*, 9527.
[66] V. Komanduri, D. J. Tate, R. Marcial-Hernandez, D. R. Kumar, M. L. Turner, *Macromolecules* **2019**, *52*, 7137.

[67] Z. A. Page, Y. Liu, E. Puodziukynaite, T. P. Russell, T. Emrick, *Macromolecules* **2016**, *49*, 2526.
[68] E. Thorn-Csányi, H.-D. Höhnk, *J. Mol. Catal.* **1992**, *76*, 101.
[69] C.-Y. Yu, M. L. Turner, *Angew. Chem. Int. Ed.* **2006**, *45*, 7797.
[70] E. Thorn-Csányi, H.-D. Höhnk, K. P. Pflug, *J. Mol. Catal.* **1993**, *84*, 253.
[71] E. Thorn-Csányi, K. P. Pflug, *Makromol. Chem.* **1993**, *194*, 2287.
[72] E. Thorn-Csányi, P. Kraxner, J. Hammer, *J. Mol. Catal.* **1994**, *90*, 15.
[73] E. Thorn-Csányi, P. Kraxner, *Macromol. Rapid Commun.* **1995**, *16*, 147.
[74] E. Thorn-Csányi, P. Kraxner, *Macromol. Chem. Phys.* **1997**, *198*, 3827.
[75] E. Thorn-Csányi, P. Kraxner, *J. Mol. Catal. A* **1997**, *115*, 21.
[76] E. Thorn-Csányi, P. Kraxner, A. Strachota, *Macromol. Rapid Commun.* **1998**, *19*, 223.
[77] R. Peetz, O. Narwark, O. Herzog, S. Brocke, E. Thorn-Csányi, *Synth. Met.* **2001**, *119*, 539.
[78] A. M. Spring, C.-Y. Yu, M. Horie, M. L. Turner, *Chem. Commun.* **2009**, 2676.
[79] B. J. Lidster, D. R. Kumar, A. M. Spring, C.-Y. Yu, M. L. Turner, *Polym. Chem.* **2016**, *7*, 5544.
[80] T. W. Funk, J. Efskind, R. H. Grubbs, *Org. Lett.* **2005**, *7*, 187.
[81] F. Menk, M. Mondeshki, D. Dudenko, S. Shin, D. Schollmeyer, O. Ceyhun, T.-L. Choi, R. Zentel, *Macromolecules* **2015**, *48*, 7435.
[82] D. R. Kumar, B. J. Lidster, R. W. Adams, M. L. Turner, *Polymer Chemistry* **2017**, *8*, 3186.
[83] D. R. Kumar, B. J. Lidster, R. W. Adams, M. L. Turner, *Macromolecules* **2018**, *51*, 4572.
[84] E. Elacqua, K. B. Manning, D. S. Lye, S. K. Pomarico, F. Morgia, M. Weck, *J. Am. Chem. Soc.* **2017**, *139*, 12240.
[85] S. Shin, F. Menk, Y. Kim, J. Lim, K. Char, R. Zentel, T.-L. Choi, *J. Am. Chem. Soc.* **2018**, *140*, 6088.
[86] C.-Y. Yu, J. W. Kingsley, D. G. Lidzey, M. L. Turner, *Macromol. Rapid Commun.* **2009**, *30*, 1889.
[87] W. Bijnens, M. Van Der Borght, J. Manca, W. de Ceuninck, L. De Schepper, D. Vanderzande, J. Gelan, L. Stals, *Opt. Mater.* **1998**, *9*, 150.
[88] S. J. Koehler, J. Hu, E. Elacqua, *Synlett* **2020**, *31*, 1435.
[89] C.-W. Chu, M. Horie, *Asian J. Org. Chem.* **2013**, *2*, 838.
[90] S.-W. Chang, M. Horie, *Chem. Commun.* **2015**, *51*, 9113.
[91] Y.-J. Lin, H.-Y. Chiang, O. Oki, S. Kushida, S.-W. Chang, S.-T. Chiu, Y. Yamamoto, T. Hosokai, M. Horie, *ACS Appl. Polym. Mater.* **2019**, *1*, 2240.
[92] M. Horie, I.-W. Shen, S. M. Tuladhar, H. Leventis, S. A. Haque, J. Nelson, B. R. Saunders, M. L. Turner, *Polymer* **2010**, *51*, 1541.
[93] C.-C. Wang, C.-Y. Yu, *Polymer* **2019**, *166*, 123.
[94] M. S. Sanford, J. A. Love, R. H. Grubbs, *J. Am. Chem. Soc.* **2001**, *123*, 6543.
[95] J. A. Love, M. S. Sanford, M. W. Day, R. H. Grubbs, *J. Am. Chem. Soc.* **2003**, *125*, 10103.
[96] S. B. Garber, J. S. Kingsbury, B. L. Gray, A. H. Hoveyda, *J. Am. Chem. Soc.* **2000**, *122*, 8168.
[97] C. W. Bielawski, R. H. Grubbs, *Prog. Polym. Sci.* **2007**, *32*, 1.
[98] P. Schwab, R. H. Grubbs, J. W. Ziller, *J. Am. Chem. Soc.* **1996**, *118*, 100.
[99] A. N. Roberts, A. C. Cochran, D. A. Rankin, A. B. Lowe, H.-J. Schanz, *Organometallics* **2007**, *26*, 6515.
[100] D. Burtscher, R. Saf, C. Slugovc, *J. Polym. Sci. A Polym. Chem.* **2006**, *44*, 6136.
[101] A. V. Ambade, S. K. Yang, M. Weck, *Angew. Chem. Int. Ed.* **2009**, *48*, 2894.

[102] S. K. Yang, A. V. Ambade, M. Weck, *J. Am. Chem. Soc.* **2010**, *132*, 1637.
[103] S. K. Chang, A. D. Hamilton, *J. Am. Chem. Soc.* **1988**, *110*, 1318.
[104] E. J. Leonhardt, R. Jasti, *Nat. Rev. Chem.* **2019**, *3*, 672.
[105] M. Ball, B. Zhang, Y. Zhong, B. Fowler, S. Xiao, F. Ng, M. Steigerwald, C. Nuckolls, *Acc. Chem. Res.* **2019**, *52*, 1068.
[106] S. E. Lewis, *Chem. Soc. Rev.* **2015**, *44*, 2221.
[107] Q. Chen, M. T. Trinh, D. W. Paley, M. B. Preefer, H. Zhu, B. S. Fowler, X.-Y. Zhu, M. L. Steigerwald, C. Nuckolls, *J. Am. Chem. Soc.* **2015**, *137*, 12282.
[108] K. Becker, E. Da Como, J. Feldmann, F. Scheliga, E. Thorn-Csányi, S. Tretiak, J. M. Lupton, *J. Phys. Chem. B* **2008**, *112*, 4859.
[109] H. Kobayashi, K. Tsuchiya, K. Ogino, M. Vacha, *Phys. Chem. Chem. Phys.* **2012**, *14*, 10114.
[110] A. Fürstner, L. Ackermann, B. Gabor, R. Goddard, C. W. Lehmann, R. Mynott, F. Stelzer, O. R. Thiel, *Chem. Eur. J.* **2001**, *7*, 3236.
[111] B. J. Lidster, S. Hirata, S. Matsuda, T. Yamamoto, V. Komanduri, D. R. Kumar, Y. Tezuka, M. Vacha, M. L. Turner, *Chem. Sci.* **2018**, *9*, 2934.
[112] T.-W. Wang, P.-R. Huang, J. L. Chow, W. Kaminsky, M. R. Golder, *J. Am. Chem. Soc.* **2021**, *143*, 7314.
[113] T.-W. Wang, M. R. Golder, *Polym. Chem.* **2021**, *12*, 958.
[114] K. Grudzień, M. Malinska, M. Barbasiewicz, *Organometallics* **2012**, *31*, 3636.
[115] V. Komanduri, D. R. Kumar, D. J. Tate, R. Marcial-Hernandez, B. J. Lidster, M. L. Turner, *Polym. Chem.* **2019**, *10*, 3497.
[116] B. J. Lidster, J. M. Behrendt, M. L. Turner, *Chem. Commun.* **2014**, *50*, 11867.
[117] F. Wang, F. He, Z. Q. Xie, Y. P. Li, M. Hanif, M. Li, Y. Ma, *Macromol. Chem. Phys.* **2008**, *209*, 1381.
[118] H. Katayama, M. Nagao, T. Nishimura, Y. Matsui, K. Umeda, K. Akamatsu, T. Tsuruoka, H. Nawafune, F. Ozawa, *J. Am. Chem. Soc.* **2005**, *127*, 4350.
[119] H. Katayama, M. Nagao, T. Nishimura, Y. Matsui, Y. Fukuse, M. Wakioka, F. Ozawa, *Macromolecules* **2006**, *39*, 2039.
[120] R. M. Moslin, C. G. Espino, T. M. Swager, *Macromolecules* **2009**, *42*, 452.
[121] M. B. Herbert, R. H. Grubbs, *Angew. Chem. Int. Ed.* **2015**, *54*, 5018.
[122] T. P. Montgomery, T. S. Ahmed, R. H. Grubbs, *Angew. Chem. Int. Ed.* **2017**, *56*, 11024.
[123] B. K. Keitz, A. Fedorov, R. H. Grubbs, *J. Am. Chem. Soc.* **2012**, *134*, 2040.
[124] R. K. M. Khan, S. Torker, A. H. Hoveyda, *J. Am. Chem. Soc.* **2013**, *135*, 10258.
[125] M. S. Mikus, S. Torker, A. H. Hoveyda, *Angew. Chem. Int. Ed.* **2016**, *55*, 4997.
[126] J.-A. Song, G. I. Peterson, K.-T. Bang, T. S. Ahmed, J.-C. Sung, R. H. Grubbs, T.-L. Choi, *J. Am. Chem. Soc.* **2020**, *142*, 10438.
[127] T.-W. Hsu, C. Kim, Q. Michaudel, *J. Am. Chem. Soc.* **2020**, *142*, 11983.
[128] T.-W. Hsu, S. J. Kempel, Q. Michaudel, *J. Polym. Sci.* **2021**, *60*, 569.
[129] V. Komanduri, Y. Janpatompong, R. Marcial-Hernandez, D. J. Tate, M. L. Turner, *Polym. Chem.* **2021**, *12*, 6731.
[130] C.-Y. Yu, S.-H. Wen, S.-H. Yu, C.-C. Wang, *J. Polym. Sci. A Polym. Chem.* **2018**, *56*, 67.
[131] U. Tritschler, S. Pearce, J. Gwyther, G. R. Whittell, I. Manners, *Macromolecules* **2017**, *50*, 3439.
[132] A. O. Moughton, M. A. Hillmyer, T. P. Lodge, *Macromolecules* **2011**, *45*, 2.

[133] C.-T. Lo, C.-J. Lin, J.-Y. Lee, S.-H. Tung, J.-C. Tsai, W.-C. Chen, *RSC Adv.* **2014**, *4*, 23002.
[134] M. Elsabahy, K. L. Wooley, *Chem. Soc. Rev.* **2012**, *41*, 2545.
[135] C. B. Braga, R. A. Pilli, C. Ornelas, M. Weck, *Biomacromolecules* **2021**, *22*, 5290.
[136] D. M. Vriezema, M. C. Aragonès, J. A. A. W. Elemans, J. J. L. M. Cornelissen, A. E. Rowan, R. J. M. Nolte, *Chem. Rev.* **2005**, *105*, 1445.
[137] R. K. O'Reilly, C. J. Hawker, K. L. Wooley, *Chem Soc Rev* **2006**, *35*, 1068.
[138] P. Qu, M. Kuepfert, M. Hashmi, M. Weck, *J. Am. Chem. Soc.* **2021**, *143*, 4705.
[139] H. Wang, H. H. Wang, V. S. Urban, K. C. Littrell, P. Thiyagarajan, L. Yu, *J. Am. Chem. Soc.* **2000**, *122*, 6855.
[140] L. zur Borg, C. Schüll, H. Frey, R. Zentel, *Macromol. Rapid Commun.* **2013**, *34*, 1213.
[141] E. Elacqua, A. Croom, D. S. Lye, M. Weck, *J. Polym. Sci. A Polym. Chem.* **2017**, *55*, 2991.
[142] S. K. Pomarico, D. S. Lye, E. Elacqua, M. Weck, *Polym. Chem.* **2018**, *9*, 5655.
[143] F. Menk, S. Shin, K.-O. Kim, M. Scherer, D. Gehrig, F. Laquai, T.-L. Choi, R. Zentel, *Macromolecules* **2016**, *49*, 2085.
[144] S. Shin, M.-L. Gu, C.-Y. Yu, J. Jeon, E. Lee, T.-L. Choi, *J. Am. Chem. Soc.* **2018**, *140*, 475.
[145] S. Shin, J. Lim, M.-L. Gu, C.-Y. Yu, M. Hong, K. Char, T.-L. Choi, *Polym. Chem.* **2017**, *8*, 7507.
[146] H. Frisch, B. T. Tuten, C. Barner-Kowollik, *Isr. J. Chem.* **2020**, *60*, 86.
[147] J. Romulus, J. T. Henssler, M. Weck, *Macromolecules* **2014**, *47*, 5437.
[148] E. Elacqua, D. S. Lye, M. Weck, *Acc. Chem. Res.* **2014**, *47*, 2405.
[149] M. Milton, R. Deng, A. Mann, C. Wang, D. Tang, M. Weck, *Acc. Chem. Res.* **2021**, *54*, 2397.
[150] C. Wang, M. Weck, *Macromol. Rapid Commun.* **2021**, *42*, 2100368.
[151] E. Elacqua, M. Weck, *Chem. Eur. J.* **2015**, *21*, 7151.
[152] J. Lu, N. ten Brummelhuis, M. Weck, *Chem. Commun.* **2014**, *50*, 6225.
[153] E. Elacqua, G. T. Geberth, D. A. Vanden Bout, M. Weck, *Chem. Sci.* **2019**, *10*, 2144.
[154] C. Resta, S. Di Pietro, M. M. Elenkov, Z. Hameršak, G. Pescitelli, L. Di Bari, *Macromolecules* **2014**, *47*, 4847.



[2.2]Paracyclophane-1,9-diene and similar strained cyclophanes are attractive monomers for the living ring-opening metathesis polymerization to afford poly(*p*-phenylene vinylene)s (PPVs) and poly(arylene vinylene)s, conjugated polymers for a wide variety of electronic and optical applications. This review examines the synthesis of alkyl and alkoxy-substituted cyclophane monomers, their polymerization reactivity using olefin metathesis catalysts, and their emerging applications in amphiphilic polymers and supramolecularly assembled architectures.