

56820-DN17: Synthesis and Dynamic Response of Responsive Shape-Persistent Ladder Polymers
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Ladder polymers represent a unique highly rigid polymer architecture, consisting of an uninterrupted series of conformationally restrictive rings. The rigid and anisotropic ladder polymer structures are expected to exhibit many properties that are quite different from common flexible linear polymers. We are interested in exploring the ladder architecture as a shape-persistent backbone for responsive polymers and polymers with large free volumes.

We recently developed an efficient ladder polymerization method based on catalytic arene-norbornene annulation (CANAL), which results in ladder polymers with contorted fused norbornyl benzocyclobutene backbones. We evaluated the functional group compatibility of CANAL reaction and incorporated useful functional groups, including hydroxyl and amino groups, into CANAL polymers (*ACS Macro Lett.* **2017**, *6*, 1357) for further manipulation of these polymers. We have observed slower CANAL in some cases where functional groups are present on bromobenzene monomers, leading to low MWs of the resulting ladder polymers. To circumvent this issue, we have prepared bisnorbornenes from CANAL of functionalized bromobenzenes using excess norbornadiene, and used these functionalized bisnorbornenes as monomers instead in CANAL polymerization, as detailed in last year's report.

In the past year, we focused on obtaining high molecular weight (MW) > 100 kDa ladder polymers in order to obtain mechanically robust solid films so that the responsive ladder polymers can be tested in solid materials. Previously, CANAL polymers with methyl substituents were limited to ~30 kDa and attempts at obtained higher MW polymers resulted in insoluble materials. We suspected that the limiting factor for MW is the solubility of rigid ladder polymers at very high MWs. We found short substituent, such as ethyl and isopropyl groups, can significantly increase the MW of resulting ladder polymers to 100-300 kDa by improving their solubility. Therefore, we subsequently used diethyl dibromobenzene as a comonomer for CANAL polymerization containing responsive monomer motifs. Alternatively, we also sought to use other polymerization methods to link CANAL ladder motifs into high MW rigid polymers. Because polyimides are commonly used robust materials for many applications, we decided to prepare high MW polyimides based on CANAL ladder motifs. We synthesized a series of CANAL diamines in high yields, which were then polymerized with (hexafluoroisopropylidene)diphthalic anhydride (6FDA), a commonly used commercial dianhydride for the synthesis of polyimides, via polycondensation (Figure 1). These polyimides had high MWs in the range of 50-150 kDa (based on polystyrene standards) and form mechanically robust films. Interestingly, we varied the backbone rigidity of these polyimides by restricting the rotation of the imide linkages using *ortho*-methyl substitutions. As we placed no to two methyl groups *ortho* to the imide bond, the measured surface areas were increased from 270 to 510 m²/g (Figure 1 top to bottom), indicating that the increased chain rigidity led to more frustrated packing and higher free volumes in the polymers.

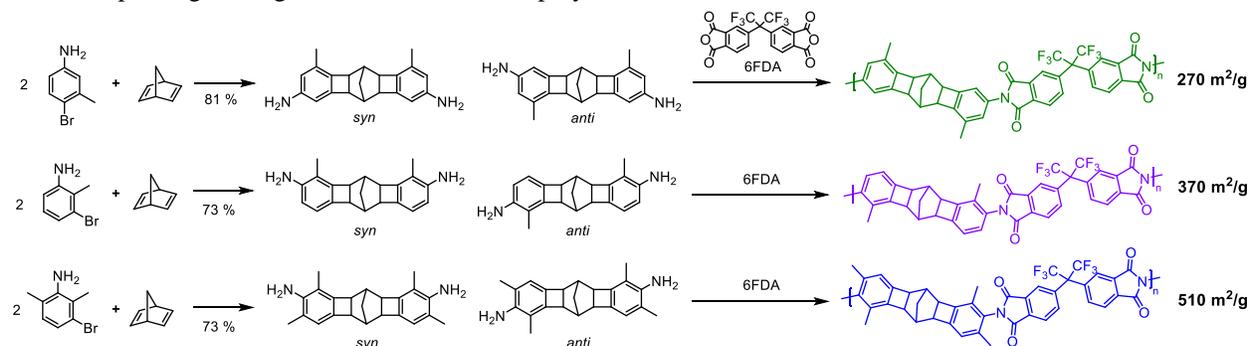


Figure 1. Synthesis of CANAL ladder diamines and CANAL polyimides.

We attempted our first design of incorporating photo-responsive motifs into ladder polymers. We chose a reported stilbene-based molecular rotor **1** from Feringa and coworkers as the responsive monomer units, because the bromo-xylene structure in **1** is ideal for CANAL polymerization and the rotor has two thermal stable state, *cis* and *trans* configurations (Figure 2). We synthesized **1** and separated the *cis* and *trans* isomers by recrystallization. We then carried out CANAL polymerization using the separated *cis*-**1** and *trans*-**1** with norbornadiene (NBD) in the presence of 1 mol% Pd(OAc)₂, 2 mol% PPh₃, and Cs₂CO₃ in THF at 130 °C for 36 h (Figure 3). Ladder polymers

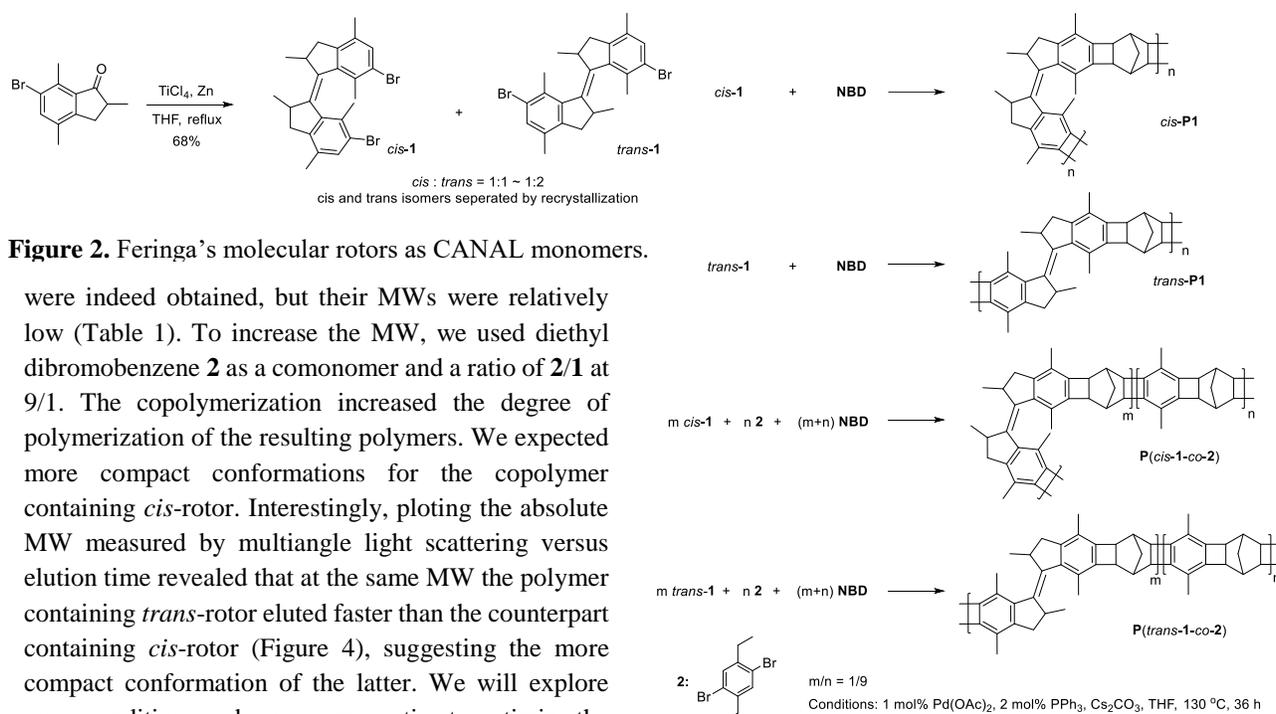


Figure 2. Feringa's molecular rotors as CANAL monomers.

were indeed obtained, but their MWs were relatively low (Table 1). To increase the MW, we used diethyl dibromobenzene **2** as a comonomer and a ratio of **2**/**1** at 9/1. The copolymerization increased the degree of polymerization of the resulting polymers. We expected more compact conformations for the copolymer containing *cis*-rotor. Interestingly, plotting the absolute MW measured by multiangle light scattering versus elution time revealed that at the same MW the polymer containing *trans*-rotor eluted faster than the counterpart containing *cis*-rotor (Figure 4), suggesting the more compact conformation of the latter. We will explore more conditions and comonomer ratios to optimize the synthesis of rotor-containing ladder polymers with high MWs. Our preliminary attempts to photo-isomerize the *cis*- and *trans*-rotor ladder polymers using 300 nm UV light resulted in decomposition of the rotor. Similar rotors based on **1** are often photoswitched by UV irradiation at low temperatures as reported by Feringa. We suspect the photo-isomerization may be slower in a polymer scaffold and prolonged irradiation at room temperature may lead to decomposition. We will explore the photo-irradiation conditions on the rotor-containing ladder polymers in the future.

Figure 3. Synthesis of rotor containing CANAL ladder (co)polymers.

Table 1. GPC Characterization of rotor containing CANAL ladder (co)polymers.

Polymer	M_n , MALLS (kDa)	M_w , MALLS (kDa)	D_M	DP^a
P1-<i>cis</i>	4	6	1.4	10
P1-<i>trans</i>	21	130	6.2	52
P(<i>cis</i>-1-co-2) <i>m/n</i> = 1/9	132	530	4.0	610
P(<i>trans</i>-1-co-2) <i>m/n</i> = 1/9	27	41	1.5	120

^aDegree of polymerization determined by the number of norbornyl units in the polymer, calculated using M_n .

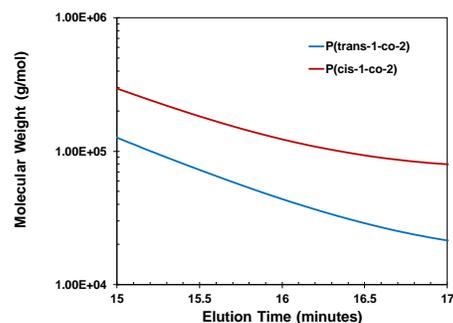


Figure 4. GPC analysis on MW vs elution time for the rotor containing CANAL ladder (co)polymers showing for extended conformation for the *trans*-rotor containing polymer.

This grant has provided partial salary support for a postdoctoral scholar to gain valuable training in small molecule and polymer synthesis and structural characterization. This work has been presented by the PI and a graduate student at an ACS meeting and a Gordon conference in 2018. Ladder polymers and microporous materials are new areas and new types of materials for the PI and many details in the synthesis and behavior of such polymers were unknown. The ACS PRF grant allowed the PI's lab to fully develop the CANAL polymerization and understand how to tune the physical properties and processing of the resulting ladder polymers. With the knowledge foundation laid with the support of this grant, synthesis, characterization, and application of ladder polymers have become a major and unique research area of the PI's lab.