Efficient Synthesis of Rigid Ladder Polymers via Palladium Catalyzed Annulation

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ⓢ *Supporting Information*

ABSTRACT: We report a new method to synthesize rigid ladder polymers using efficient palladium catalyzed annulation reactions with low catalyst loading (1 mol %). Rigid ladder polymers with benzocyclobutene backbone linkages can be synthesized from copolymerization of readily accessible aryl dibromides and norbornadiene or polymerization of AB type monomers bearing norbornene and aryl bromide or triflate moieties. High molecular weight (10−40 kDa) rigid ladder polymers can be obtained with complete monomer conversions. Diverse monomers also gave different, fixed ladder polymer conformations. The ladder polymers exhibited excellent thermal stability, high carbonization yield, and large intrinsic porosity.

A central challenge in polymer chemistry is to precisely and efficiently control polymer architectures, which strongly influence the physical properties and applications of polymeric materials. In contrast to conventional polymers connected by single bonds, ladder polymers represent a unique architecture, where each repeat unit is connected by two bonds,[1,2] resulting in much more restricted chain conformations. Rigid ladder polymers have recently been shown to be very promising materials for efficient gas separation, and the high rigidity was critical for selectivity in gas separation.[3,4] We also envision a wide range of applications for rigid ladder polymers resulting from the high anisotropy and intrinsic porosity, including dielectric materials and nanostructured materials. However, very few methods exist to synthesize ladder polymers by simultaneous formation of two-bond linkages. Schlüter and Swager groups pioneered the synthesis of ladder polymers via Diels−Alder reactions,[5−7] but the polymerizations required very high pressure and/or temperature. McKeown and Budd groups recently developed ladder polymer synthesis based on Tröger's base formation[4,8] and double aromatic nucleophilic substitution.[3,9] Multistep monomer syntheses were often required and no stereocontrol could be achieved in the few reported methods.

We became interested in exploring powerful and versatile transition metal catalysis to synthesize novel polymers from readily accessible building blocks. Transition metal catalysis has continuously stimulated the emergence of new polymer chemistry to gain access to novel polymers and new materials.[10−14] New catalytic methods also enabled diverse monomers to be used for the synthesis of new types of polymers.[15−18] Herein, we report the first catalytic synthesis of rigid ladder polymers in nearly quantitative conversions using efficient Pd catalyzed annulation reaction.

Catellani and co-workers explored Pd catalyzed reactions between aryl bromides and norbornene (NB).[19] A stable palladacycle **1** from C−H activation on the arene can be formed in the catalytic cycle, which can undergo reductive elimination to form an interesting benzocyclobutene (BCB) product **2**,[20−23] as well as undergo pathways **B** and **C**, leading to other products (Scheme 1).[19] Although rarely explored in small molecule

Scheme 1. Pd Catalyzed Annulation: Possible Products and Selectivity
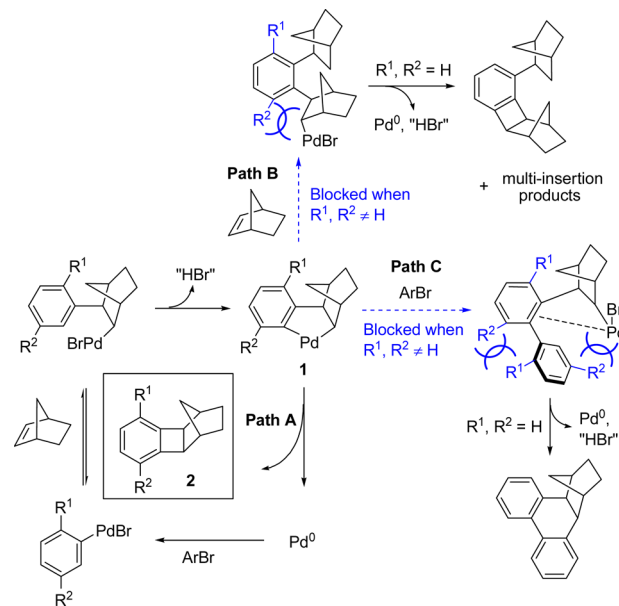
synthesis[20−23] and never in polymer synthesis, we were intrigued by the BCB product and envisioned it as a novel motif to build rigid ladder polymers. Furthermore, we hypothesized that blocking the 2,5-positions of the aryl halide may inhibit the reaction pathways **B** and **C** due to steric congestion and give only the desired BCB product. Exclusive selectivity and high efficiency for the annulation pathway is a prerequisite to utilize this reaction for polymer synthesis.
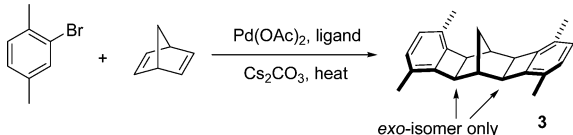
Our initial attempt on a model reaction between 2-bromotoluene and norbornadiene (NBD) using 10 mol % Pd(PPh₃)₄ and K₂CO₃ resulted in complete consumption of

starting materials but led to complex product mixtures. To test our hypothesis of blocking reaction pathways **B** and **C**, we started with commercially available 2,5-dimethyl-bromobenzene and NBD. Gratifyingly, after initial optimization, the desired BCB product **3** was formed in >98% conversion using Pd(OAc)$_2$, PPh$_3$, and Cs$_2$CO$_3$ at 130 °C, and the reaction was highly stereoselective with exclusively the *exo*-isomer formed, as indicated by the nuclear Overhauser effect (NOE) experiment (see Supporting Information (SI) Figure S4). The reaction was sensitive to the sterics of the phosphine ligand as bulkier ligands gave lower conversions (Table 1, entry 3–4). *N*-Heterocyclic

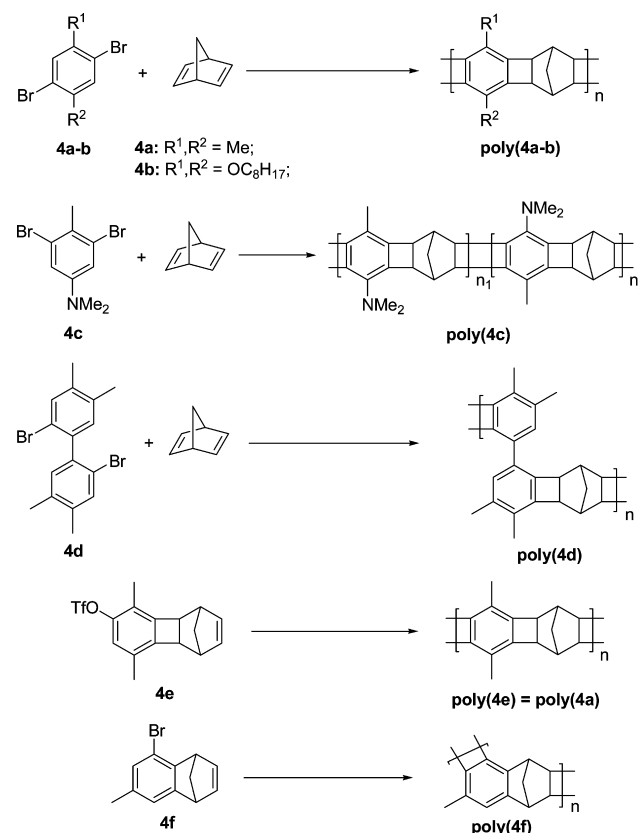### Table 1. Optimization of a Model Reaction for Ladder Polymerization[a]

exo-isomer only   **3**

entry	ligand	temp (°C)	cat (mol %)[b]	conv (%)[c]
1	PPh$_3$	130	5	>98
2	PCy$_3$	130	5	94
3	PtBu$_3$	130	5	68
4	P(o-Tol)$_3$	130	5	<5
5	NHC[d]	130	5	<5
6	PPh$_3$	115	5	>98
7	PPh$_3$	100	5	80
8	PPh$_3$	115	1	>98
9[e]	PPh$_3$	115	0.1	91
10[f]	PPh$_3$	115	0.1	>98

[a]Reactions were performed using Pd(OAc)$_2$, 2 equiv of ligand to Pd, and 1 equiv Cs$_2$CO$_3$, at [NBD] = 0.1 M in toluene for 5 h in a sealed tube, unless otherwise noted. [b]Based on the mole ratio of Pd to halide. [c]Determined by ^{1}H NMR of crude reaction mixture. [d]PEPPSI-IPr Pd catalyst used. [e]Reaction run for 24 h. [f]Reaction run in THF for 24 h.

carbene (NHC) based PEPPSI catalyst, although highly efficient in many cross-coupling reactions,[24] gave very low conversion (Table 1, entry 5). Under optimized conditions, we could lower the catalyst loading to only 0.1 mol % and reaction temperature to 115 °C and still obtain 91% and complete conversions to **3** in toluene and THF, respectively, after 24 h. The turnover number (TON) was measured to be 1176 and turnover frequency (TOF) to be 49 h^{-1}. The low catalyst loading and the absence of detectable side reactions open the door for the application of this annulation reaction to polymer chemistry and scalable materials synthesis.

We next proceeded with polymerization of NBD and various aryl dibromides (Table 2). Polymers were obtained with complete monomer conversions for attempted aryl dibromides **4a–d**. The resulting ladder polymers can be dissolved in THF, and their absolute MW was measured by gel permeation chromatography (GPC) coupled with a multiangle laser light scattering (MALLS) detector. The efficient polymerization resulted in ladder polymers with high MWs in the range of 10–40 kDa and relatively narrow, monomodal MW distribution (Table 2 and Figure 1). The high MW and relatively low PDI are particularly gratifying since the polymerization is presumably step-growth polymerization. ^{1}H and ^{13}C NMR spectroscopy indicated exclusive BCB ladder backbone linkage and the expected end group signals of the olefin from NB and of the arene protons from aryl bromide and debrominated arene

Table 2. Synthesis of Various Benzocyclobutene Ladder Polymers

4a-b   **4a**: R^1,R^2 = Me;   **poly(4a-b)**
      4b: R^1,R^2 = OC$_8$H$_{17}$;

4c   **poly(4c)**

4d   **poly(4d)**

4e   **poly(4e) = poly(4a)**

4f   **poly(4f)**

entry[a]	monomer(s)	$M_n{}^b$ (kDa)	PDI[b]	DP[c]
1	**4a** + NBD	29	1.38	150
2	**4b** + NBD	13	1.34	31
3	**4a/4b** (9:1) + NBD	16	1.58	52
4	**4c** + NBD	36	1.36	160
5[d]	**4d** + NBD	13	1.66	44
6[e]	**4e**	12	1.28	62
7[d]	**4f**	14	1.28	91

[a]Reaction was conducted using 1 mol % Pd(OAc)$_2$, 2 mol % PPh$_3$, and 1 equiv of Cs$_2$CO$_3$, at [monomer] = 0.5 M in toluene at 115 °C for 24 h in a sealed tube, unless otherwise noted. [b]Determined by GPC MALLS analysis in THF. [c]Degree of polymerization = M_n/MW of repeat unit. [d][monomer] = 1.0 M, reaction run for 12 h. [e]Reaction run in THF.
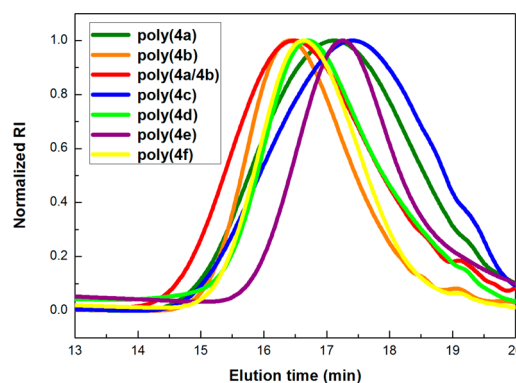

Figure 1. GPC traces of synthesized ladder polymers in Table 2.

(Figure 2 and see SI). The resulting ladder polymers are generally soluble in nonpolar solvents, such as THF, DCM, and
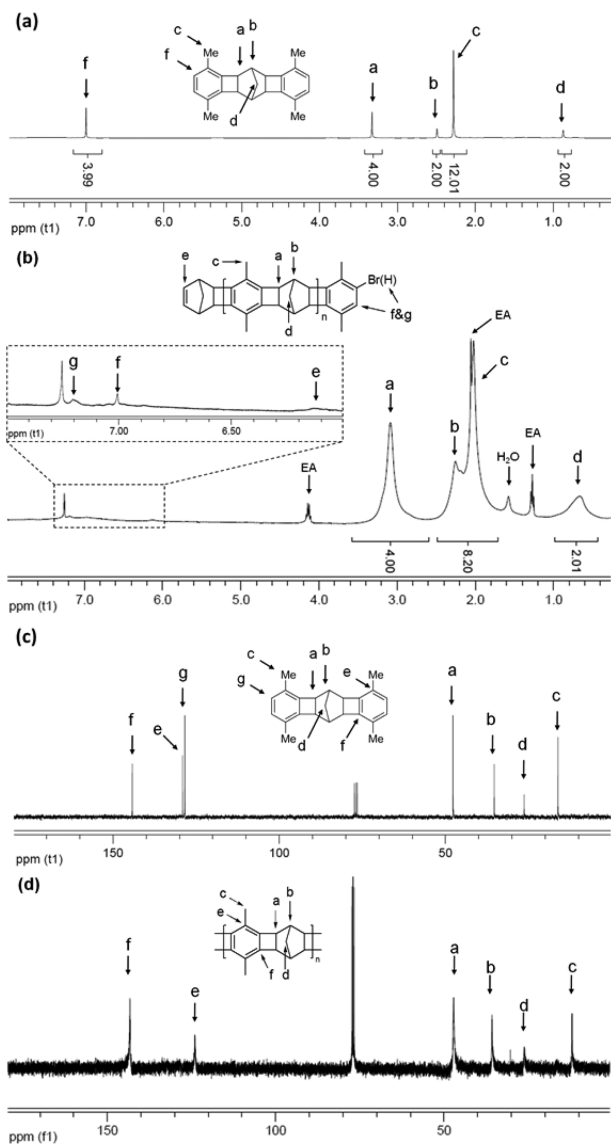

Figure 2. ^{1}H NMR spectra of model compound **3** (a) and **poly(4a)** (b); ^{13}C NMR spectra of model compound **3** (c) and **poly(4a)** (d) with their assignments in CDCl$_3$.

chloroform. Uniquely, the straight BCB linkage keeps the backbone of **poly(4a−c)** in a bowing-ribbon conformation (Figure 3). The overall polymer chain may resemble a disc shape, which we plan to study in future scattering experiments. The biphenyl monomer **4d** represents one type of easily accessible monomers that can give the resulting ladder polymers a certain degree of bending freedom in two dimensions resulting from the restricted biphenyl bond (Figure 3). Furthermore, these polymers can be synthesized on gram scale thanks to the facile access to a large number of aryl bromides, paving the way for their materials applications.

To eliminate the need for precise loading of 1:1 ratio of AA and BB types of monomers for step-growth polymerization, we also synthesized AB-type monomers **4e** and **4f** that contain NB and aryl triflate or bromide groups. Both **4e** and **4f** polymerized with no detectable monomer remaining and produced the expected
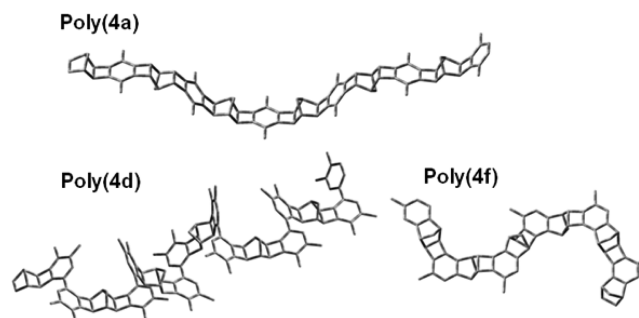

Figure 3. Minimum energy segment (6 repeat units) conformations of ladder polymers, **poly(4a)**, **poly(4d)**, and **poly(4f)**, using molecular dynamics simulation.

ladder backbones as indicated by ^{1}H and ^{13}C NMR spectra (see SI). Their polymerizations needed to be stopped after 12 h to ensure the polymer's solubility in THF for GPC characterization. Prolonged polymerizations of **4e** and **4f** resulted in polymers that were only soluble in chloroform, which presumably had higher MW. Interestingly, monomer **4f** induces a fixed bending angle of ~120° at each repeating unit of **poly(4f)**, resulting in a kinked ribbon backbone conformation (Figure 3). The kinked ribbon backbone results in a more expanded conformation. This was evidenced from comparing the GPC traces of **poly(4e)** and **poly(4f)**, which have similar absolute MW and PDI (M_n = 12 and 14 kDa, respectively), but **poly(4f)** clearly shifted to an earlier elution time (Figure 1), indicating its larger hydrodynamic volume than that of **poly(4e)**.

In addition, we were also able to synthesize ladder polymers with only NB end groups, when NB was intentionally used in 10 mol % excess to aryl bromide (see SI Figure S25). NB is a convenient reactive group that can be used for cross-linking or synthesizing block copolymers.

The rigid, nonconjugated ladder backbone renders these polymers' interesting properties. We took polymer **poly(4a)** as an example for detailed property investigation. Differential scanning calorimetry (DSC) analysis of **poly(4a)** showed no phase transition up to 200 °C, indicating extremely glassy backbone. Thermal gravimetric analysis (TGA) indicated that the polymer was stable up to 315 °C, and lost only 14% weight at 496 °C, which we attributed to the loss of the two methyl substituents. Upon further heating under argon, this polymer can be carbonized with nearly 81% mass retention at 800 °C (see SI Figure S1). In comparison, a common carbon precursor polymer, polyacrylonitrile, has a carbonization yield around 50%.[25] The very high carbonization yield of **poly(4a)** is a result of the high degree of unsaturation of the polymer. Furthermore, frustrated packing of rigid ladder chains resulted in large intrinsic porosity with the surface area of 620 m^2/g for **poly(4a)** measured by Brunauer−Emmett−Teller (BET) analysis (see SI Figure S2). We also performed density functional theory (DFT) calculations (B3LYP/6-31G* basis set) on the bond angle between BCB and NB motifs. The rapidly increasing energy barrier to the bond bending suggested high rigidity for the BCB linkage (see SI Figure S3). The combined solubility, thermal stability, high rigidity, and large porosity may make robust BCB−NB ladder polymers promising materials for a range of engineering applications.

In summary, we report efficient synthesis of rigid ladder polymers via Pd catalyzed annulation between various readily available aryl bromides and NBD. We found blocking accessibility of other reaction pathways produced ladder

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dx.doi.org/10.1021/ja5110415 | *J. Am. Chem. Soc.* 2014, 136, 17434−17437

polymers with rigid BCB linkage in quantitative conversions at low catalyst loading. We are currently expanding monomer scopes to control polymer conformation and porosity and characterizing the long-range chain conformations. Exploration of these ladder polymers' applications is also underway.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental details, ^{1}H and ^{13}C NMR spectra, TGA and BET characterizations, and calculated bending barrier for the ladder linkage. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes
The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

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