Title
Initiator Control of Conjugated Polymer Topology in Ring-Opening Alkyne Metathesis Polymerization

Permalink
https://escholarship.org/uc/item/3cs2v2pf

Journal
Journal of the American Chemical Society, 138(19)

ISSN
0002-7863

Authors
Von Kugelgen, S
Bellone, DE
Cloke, RR
et al.

Publication Date
2016-05-18

DOI
10.1021/jacs.6b02422

Peer reviewed
Initiator Control of Conjugated Polymer Topology in Ring-Opening Alkyne Metathesis Polymerization


†Department of Chemistry, University of California Berkeley, Berkeley, California 94720, United States
‡Materials Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, California 94720, United States
§Kavli Energy Nanosciences Institute at the University of California Berkeley and Lawrence Berkeley National Laboratory, Berkeley, California 94720, United States

ABSTRACT: Molybdenum carbyne complexes [RC=Mo(OC(CH3)(CF3)2)] featuring a mesityl (R = Mes) or an ethyl (R = Et) substituent initiate the living ring-opening alkyne metathesis polymerization of the strained cyclic alkyne, 5,6,11,12-tetradehydrobenzo[4,5][8]annulene, to yield fully conjugated poly[(o-phenylene ethynylene)]. The difference in the steric demand of the polymer end-group (Mes vs. Et) transferred during the initiation step determines the topology of the resulting polymer chain. While [Mes=Mo(OC(CH3)(CF3)2)] exclusively yields linear poly[(o-phenylene ethynylene)], polymerization initiated by [EtC=Mo(OC(CH3)(CF3)2)] results in cyclic polymers ranging in size from n = 5 to 20 monomer units. Kinetic studies reveal that the propagating species emerging from [EtC=Mo(OC(CH3)(CF3)2)] undergoes a highly selective intramolecular backbiting into the butynyl end-group.

Semiconducting π-conjugated polymers have been widely explored as functional materials in advanced electronic devices. They combine the superior processability and mechanical performance of polymers with readily tunable optical, electrical, and magnetic properties of small molecules. Applications for these polymers include electronic devices such as organic photovoltaics (OPVs),4,5 organic light-emitting diodes (OLEDs),6,7 organic field-effect transistors (OFETs),8,9 photorefractive devices,7 and environmental sensors.10-12 Among these materials, poly[(o-phenylene ethynylene)] (PPE), a class of conjugated polymers featuring a pattern of alternating aromatic rings and triple bonds, have stood out for their fully conjugated nature, moderate fluorescence quantum yields,13,14 and readily tunable band gap.15,16 The macromolecular assembly of PPEs in solution and thin films can be tuned from densely packed linear organizations to well defined helical coiled or zig-zag structures17 by varying the substitution pattern (para-, meta-, ortho-) of the aromatic rings along the backbone of the polymer chain. The classical syntheses of PPEs rely on step-growth polymerizations based on either transition metal catalyzed cross-coupling reactions or alkyn cross-metathesis (ACM).18,19 While ACM and cyclodepolymerization of linear polymers have previously been used to access cyclic topologies, the thermodynamic products of these reactions are usually small cyclic oligomers comprised of not more than 3–6 alkenes.20-24 Transition-metal catalyzed cross-coupling polymerizations of aryl halides with aromatic alkynes, instead, suffer from undesired termination reactions, e.g. dehalogenation, and structural defects along the polymer backbone such as butadiyne groups emerging from oxidative coupling of terminal alkynes. While these strategies benefit from readily accessible monomers, they lack the precise control over degree of polymerization, molecular weight, end-group functionality, and polydispersity unique to a controlled ring-opening alkyne metathesis polymerization (ROAMP) mechanism.25-27

In this study we report a novel route towards fully conjugated PPE based on two ROAMP catalysts [Mes=Mo(CO)(CH3)(CF3)2] and [EtC=Mo(CO)(CH3)(CF3)2(DME)] (DME = 1,2-dimethoxyethane) 2 (Scheme 1) that selectively yield PPE featuring either linear or cyclic polymer topology. Both catalysts rapidly initiate the polymerization of ring-stained monomer 5,6,11,12-tetradehydrobenzo[4,5][8]annulene (3) to form poly[(ortho-phenylene ethynylene)] (PoPE) featuring a mesityl or an ethyl end-group, respectively. Time-resolved NMR spectroscopy reveals that the active chain ends of the polymers featuring a mesityl end-group are stable under the reaction conditions. In the absence of monomer, living polymers formed from 2 instead undergo highly regioselective backbiting into the least sterically hindered alkyne (EtC≡C) at the end-group to give cyclic PoPE with n > 5 and the starting catalyst 2. We herein demonstrate an unprecedented structural control over polymer topology by taking advantage of the unique selectivities of two ROAMP catalysts to form either linear or cyclic fully conjugated polymers derived from ring-stained monomers.

RESULTS AND DISCUSSION

Catalyst 1 was synthesized from Mo(CO)5 and MesLi following a procedure described by Tamm.28 The DME adduct of catalyst 2 was obtained through cross-metathesis of the nitrido-complex [N=Mo(CO)(CH3)(CF3)2] with hex-3-yne as described by Johnson.29 Orange prisms of 2 suitable for X-ray crystallography were obtained from a saturated toluene solution at ~35 °C. The geometry at the Mo center is pseudo-octahedral. X-ray crystallography of 2 (Figure 1) confirms the presence of a C(1)=Mo(1) triple bond...
with a bond length of 1.736(2) Å and a C(2)–C(1)–Mo(1) angle of 176.44(19)°. Three hexafluoro-tert-butoxide ligands adopt a meridional conformation featuring typical Mo(1)–O(1), Mo(1)–O(2), and Mo(1)–O(3) distances of 1.9632(15) Å, 1.9326(15) Å and, 1.9720(15) Å. In the crystal structure one equivalent of DME is coordinated to the Mo complex. The bond distances are 2.2283(15) Å and 2.4526(15) Å for the Mo(1)–O(4) cis and Mo(1)–O(5) trans to the carbyne, respectively. In solution the octahedral complex 2 is in dynamic equilibrium with the pentacoordinate monodentate DME complex and the fully DME dissociated tetracoordinate complex.30 At 24 °C in benzene, the equilibrium lies on the side of the associated complexes 2 (Kd = 6.2 × 10⁻³ mol L⁻¹) (Supporting Information Figure S1). Variable temperature NMR reveals that the exchange is fast suggesting that an open coordination site is readily available to bind the alkyne substrate.

**Figure 1.** ORTEP representation of the X-ray crystal structure of 2. Thermal ellipsoids are drawn at the 50% probability level. Color coding: C (gray), O (red), F (green), Mo (turquoise). Hydrogen atoms are omitted for clarity.

**Scheme 1.** Synthesis of linear poly-3a and cyclic poly-3b from ring strained monomer 3 using ROAMP catalyst 1 and 2.

We studied the ROAMP of 5,6,11,12-tetradehydrobenzo[a,e][8]annulene (3) with 1 and 2 (Scheme 1).31 Addition of 1 to a solution of 3 (50 mM) in toluene ([3]/[1] = 10) at 24 °C leads to the precipitation of polymers within 1 hour. ¹H and ¹³C NMR indicate that 1 quantitatively initiates with a half-life of t₁/₂ ≪ 1 min to form the propagating species. Monomer 3 is consumed in less than 1 h at 24 °C. The active ROAMP catalyst remains attached to the growing polymer chain. The molecular weight of the resulting polymers scales linearly with monomer conversion (Supporting Information Figure S2).

**Table 1.** Molecular weight analysis of poly-3a.

<table>
<thead>
<tr>
<th>[3]/[1]</th>
<th>Mₙ</th>
<th>Mₘ</th>
<th>Mₚ</th>
<th>Xₚ</th>
<th>PDI</th>
</tr>
</thead>
<tbody>
<tr>
<td>10/1</td>
<td>2134</td>
<td>1700</td>
<td>3000</td>
<td>11</td>
<td>1.7</td>
</tr>
<tr>
<td>20/1</td>
<td>4134</td>
<td>4800</td>
<td>6400</td>
<td>21</td>
<td>1.3</td>
</tr>
<tr>
<td>30/1*</td>
<td>6134</td>
<td>6600</td>
<td>9400</td>
<td>29</td>
<td>1.4</td>
</tr>
</tbody>
</table>

* [3]/[1] loadings > 30 lead to precipitation of insoluble polymers before all monomer is consumed; * calibrated to narrow polydispersity polystyrene standards; * degree of polymerization determined by ¹H NMR end-group analysis.

Precipitation of the resulting polymer with MeOH affords poly-3a in 82% isolated yield. Gel permeation chromatography (GPC) analysis for various [3]/[1] loadings at 24 °C in toluene shows a PDI of 1.3–1.7 (Table 1). The molecular weights of poly-3a determined by GPC, calibrated to polystyrene standards, scale with the conversion of monomer, are proportional to the initial [3]/[1] loading and show a unimodal distribution (Figure 2a). Extended reaction times do not lead to a broadening of the PDI. Mass spectrometry of polymers that have been quenched with MeOH is consistent with the characteristic signature for one mesityl end-group and a statistical mixture of CH₃, CH₂OH, or CHO end-groups resulting from the cleavage of the propagating molybdenum carbyne species (Supporting Information Figure S3). While the ¹H...
Figure 3. ROAMP of isotopically labeled 3* with catalyst 1 (A) and 2 (B) followed by time resolved 1H, 19F, and 13C NMR spectroscopy. Mole fraction of transient intermediates during the reaction of 1 (C) and 2 (D) with 3 derived from 1H NMR. Isotopic labeling: * 99.5% 13C, • 50% 13C.

To gain insight into the reaction mechanism we studied the ROAMP of 13C-labeled 3* with 1. In the presence of monomer the resting state of the catalyst observed by 13C NMR is the interconverting metallacyclobutadienes 1a and 1b (Figure 3a, Supporting Information Figure S6,S8) characterized by two broad sets of 1H and 19F resonances for the alkoxides (axial and equatorial) and two sets of 13C resonances for the metallacyclobutadiene carbons (one β carbon and two α carbons).30,31 Following the consumption of 3* the metallacyclobutadiene 1b undergoes a final cycloreversion to give the labeled, ring-opened molybdenum benzylidyne complex 1c. In the absence of monomer, 1c is stable for > 10 h and remains attached to one end of the polymer chain pending MeOH solvolysis. If the same polymerization is performed with 2, the dominant molybdenum species observed in 13C NMR are the interconverting metallacyclobutadienes 2a and 2b (Figure 3b, Supporting Information Figure S7,S9). Following the consumption of monomer, 2b undergoes a final cycloreversion to give the ring-opened molybdenum benzylidyne complex 2c. While 1c is stable in the reaction mixture, 2c undergoes highly regioselective backbiting into the butynyl end-group to give cyclic poly-3b and the original unlabeled molybdenum propylidyne complex 2. The outstanding selectivity of this backbiting reaction is reflected in the absence of half-integer multiples of the monomer (m/z = [n x 200 + 100] g mol⁻¹) in the mass spectrum of poly-3b (Figure 2b). The increased steric demand of internal alkynes lining the backbone of the growing polymer chain (2c) prevents a stochastic backbiting process and directs 3b. GPC analysis of samples prepared from various [3]/[2] loadings at 24 °C in toluene indicates the formation of discrete cyclic oligomers (poly-3b) and some higher molecular weight linear polymers (Mn = 5,000–10,000) resulting from intermolecular cross-metathesis of living polymer chains. The ratio of products emerging from an intra- vs. intermolecular chain transfer is concentration dependent ranging from 93% cyclic polymers at [2] = 1 mM to 86% at [2] = 10 mM as determined by 1H NMR (Supporting Information Table S1, Figure S4,S5). The linear polymers can be removed by Soxhlet extraction or fractional precipitation to give pure cyclic poly-3b in > 60% isolated yield (Figure 2a). Mass spectrometry of poly-3b shows evenly spaced peaks corresponding to integer multiples of 3 (m/z = [n x 200] g mol⁻¹, n = 5, 6, 7, ..., 20; Figure 2b). The absence of end-groups in poly-3b is further corroborated by 1H and 13C NMR spectroscopy (Supporting Information Figure S15,S16) and highlights the unusual selectivity of catalyst 2 for the formation cyclic poly-3b over linear poly-3a.
the reaction exclusively towards the unhindered butynyl end-group. Kinetic studies using 
\[ \text{TolC}=\text{Mo(OC(CH}_{3})_{3}(CF}_{3})_{3}(\text{DME}) \] (4) as a model complex for the propagating species 2c, show that the rate of cross-metathesis with the sterically less demanding 1-(but-1-
yn-1-yl)-2-methylbenzene (5a) is ~200 times faster (k = 1.3 × 10^{-5}
M^{-1}s^{-1}) than with 1,2-bis(o-toly)acetylene (5b) (k = 7.1 × 10^{-4}
M^{-1}s^{-1}) (Supporting Information Figure S10, S11). The subtle kinetic selectivity that directs the intramolecular cross-metathesis of 2c toward the sterically less hindered butynyl end-group has previously been observed for acyclic diyne metathesis (ADMET).^{21}

The topological difference of linear and cyclic polymers, poly-3a and poly-3b, is reflected in their photophysical properties. Although the UV-Vis absorption spectra of poly-3a and poly-3b appear similar (Figure 4), cyclic poly-3b exhibits a higher fluorescence quantum yield upon excitation at 300 nm (ΦF = 8.4% and 18.6% for poly-3a and poly-3b, respectively). As the emission spectrum does not shift to longer wavelengths, the observed enhancement cannot be explained by the formation of excimer complexes between adjacent monomer units as has been observed for e.g. cyclic polystyrene.\(^{35}\) Instead, enhanced quantum yield can be attributed to the reduced conformational entropy of cyclic poly-3b. Cyclic poly-3b experiences less nonradiative relaxation than linear poly-3a due to the restricted intramolecular rotation about the polymer backbone.\(^{36,37}\) The unique control over polymer topology enables tuning the mechanical and photophysical properties of PolPFs with minimal effect on their electronic structure.

**CONCLUSION**

We describe the synthesis of a fully conjugated poly(o-phenylene
ethenylene) using living ring-opening alkylene metathesis poly
erization. Tuning the steric demand of the molybdenum carbony
initiator directs the synthesis of either linear or cyclic polymers with
high selectivity. The polymerization mechanism and catalyst rest
ning states were investigated through multinuclear NMR kinetic and
\(^{13}C\) labeling studies. The catalyst system described herein repres
ents an extraordinary access to the field of conjugated organic
materials, simultaneously enabling exceptional control over poly
mer structure, sequence and topology.

**EXPERIMENTAL SECTION**

**Materials and General Methods.** Unless otherwise stated, all ma
nipulations of air and/or moisture sensitive compounds were car
ried out in oven-dried glassware, under an atmosphere of Ar or N2.
All solvents and reagents were purchased from Alfa Aesar, Spec
trum Chemicals, Acros Organics, TCI America, and Sigma-Aldrich
and were used as received unless otherwise noted. Organic solvents
were dried by passing through a column of alumina and were de
gassed by vigorous bubbling of N2 or Ar through the solvent for 20
min. Flash column chromatography was performed on SiCylcide
silica gel (particle size 40–63 μm). Thin layer chromatography was
carried out using SiCylcide silica gel 60 Å F-254 precoated plates
(0.25 mm thick) and visualized by UV absorption. All 'H, ('H)\(^{13}\)C,
and \(^{19}F\) NMR spectra were recorded on Bruker AV-600, DRX-500,
and AV-500 spectrometers, and are referenced to residual solvent
peaks (CDCl\(_3\), \(^{1}H\) NMR δ = 7.26 ppm, \(^{13}C\) NMR δ = 77.16 ppm;
C\(_6\)D\(_6\), \(^{1}H\) NMR δ = 7.16 ppm, \(^{13}C\) NMR δ = 128.06 ppm; Tol-d\(_{5}\),
\(^{1}H\) NMR δ = 2.08 ppm; THF-d\(_{8}\), \(^{1}H\) NMR δ = 1.78 ppm, \(^{13}C\) NMR δ =
67.21 ppm) or hexafluorobenzene (\(^{19}F\) NMR δ = -162.90 ppm).
The concentrations of 4, 5a, and 5b were determined by \(^{1}H\) and \(^{19}F\) NMR using the ERETIC method\(^{48}\) against an external standard of
18.2 mM 1,3,5-tris(trifluoromethyl)benzene in C\(_6\)D\(_6\). ESI mass spec
rometry was performed on a Finnigan LTQ FT (Thermo) spectrometer in positive ionization mode. MALDI mass spectrometry was performed on a Voyager-DE PRO (Applied Biosystems Voyager System 6322) in positive mode using a matrix of dithranol. Elemental analysis (CHN) was performed on a Perkin Elmer 2400 Series II combustion analyzer (values are given in %). Gel permeation chromatography (GPC) was carried out on a LC/MS Agilent 1260 Infinity set up with a guard and two Agilent PolyPore 3 column (7.5 mm columns at 35 °C. All GPC analyses were performed on a 0.2 mg/mL solution of polymer in chloroform. An injection volume of 25 μL and a flow rate of 1 mL/min were used. Calibration was based on narrow polydispersity polystyrene standards ranging from \(M_n = 100\) to 4,068,981. X-ray crystallography was performed on APEX II QUAZAR, using a Microfocus Sealed Source (Incoatec IµS; Mo-Ka radiation), Kappa Geometry with DX (Bruker-AXS build) goniostat, a Bruker APEX II detector, QUAZAR multi
layer mirrors as the radiation monochromator, and Oxford Cryostream 700 for 2. Crystallographic data was refined with SHEXL-L97, solved with SIR-2007, visualized with ORTEP-32, and finalized with WinGX. UV-Vis absorption spectra were acquired in chloroform solution on a Varian Cary 50 spectrophotometer (Agilent, USA). Fluorescence emissions spectra were acquired at an excitation wavelength of 300 nm on a Fluoromax-4 spectrofluorometer equipped with automatic polarizers, 1.0 nm slt widths for excitation/emission and a 0.5 s integration time. Quantum yields were calibrated to 1,4-bis(5-phenyloxazol-2-yl) benzene (POPOP) in cyclohexane (ΦF = 0.97).\(^{71}\) 1,2,3,4,4',4''-pentabenzyl (5b) were synthesized following literature procedures.

**Preparation of 4**

Preparation of 4. 100 mL sealable Schlenk flask was charged under N\(_2\) with\(\text{NaMO(OC(CF}_{3})_{3}(\text{CH}_{3})\) (1.00 g, 1.53 mmol) and 3-hexyne (1.25
g, 15.22 mol) in toluene (50 mL) and heated to 95 °C for 20 h. The reaction mixture was cooled to 24 °C, 1,2-dimethoxyethane (156 mg, 1.73 mmol) was added, and stirred for 30 minutes. The solvent was removed under vacuum. The residue was extracted with Et\(_2\)O (20 mL), filtered through Celite, concentrated to 5 mL under vacuum and cooled to ~35 °C. The precipitate was collected by filtration. Recrystallization from pentane (~35 °C) yielded 2 (0.69 g, 0.90 mmol, 58%). Crystals for X-ray analysis were grown from toluene. 'H NMR (600 MHz, C\(_6\)D\(_6\) , 22 °C) δ = 3.16 (s, 6H, (CH\(_3\)OCH\(_3\))\(_2\)), 3.00 (s, 4H, (CH\(_3\)OCH\(_3\))\(_2\)), 2.65 (q, \(J\) = 7.6 Hz, 2H, MoCCH\(_3\)), 1.71 (s, 9H, OC(\(\text{CF}_{3}\))\(_3\)), 1.09 (s, \(J\) = 7.6 Hz, 3H, MoCCH\(_3\)), ppm; \(^{13}C\) NMR (151 MHz, C\(_6\)D\(_6\), 22 °C) δ = 309.8 (MoC\(_7\)), 124.5 (q, \(J\)\(_{CF}\) = 289 Hz, OC(\(\text{CF}_{3}\))\(_3\)), 83.3 (m,
**ACKNOWLEDGMENT**

Research supported by the National Science Foundation under contract number CHE-1455289, Berkeley NMR Facility is supported in part by NIH grant SRR023679A, and X-Ray Facility is supported in part by NIH Shared Instrumentation Grant 1S10-RR027172. D.E.B. acknowledges fellowship support through the Abramson Foundation. The authors acknowledge Dr. Christian Canlas and Dr. Hasan Celik for support with NMR acquisition and Dr. Antonio DiPasquale for assistance with X-ray analysis.

**REFERENCES**

Bellone, D. E.; Bours, J.; Menke, E. H.; Fischer, F. R. J. Am. Chem. Soc. 2015, 137 (2), 850–856. Strained 5,6,11,12-tetradehydrobenzo[a,e][8]annulene (3) decomposes rapidly at $T > 40 \degree C$ and was thus incompatible with the ROAMP catalyst reported in reference 31.


Table of Contents Artwork