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Ring Expansion Alkyne Metathesis Polymerization

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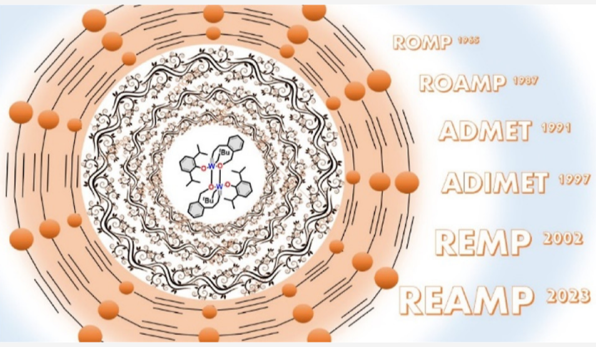
ABSTRACT: The synthesis, characterization, and preliminary activity of an unprecedented tethered alkylidyne tungsten complex for ring expansion alkyne metathesis polymerization (REAMP) are reported. The tethered alkylidyne **7** is generated rapidly by combining alkylidyne $W(C^tBu)(CH_2{}^tBu)(O\text{-}2,6\text{-}i\text{-}Pr_2C_6H_3)_2$ (**6**) with 1 equiv of an yne-ol proligand (**5**). Characterized by NMR studies and nuclear Overhauser effect spectroscopy, complex **7** is a dimer. Each metal center contains a tungsten−carbon triple bond tethered to the metal center via an alkoxide ligand. The polymerization of the strained cycloalkyne 3,8-didodecyloxy-5,6-dihydro-11,12-didehydrodibenzo-[*a*,*e*]-[8]annulene, **8**, to generate cyclic polymers was demonstrated. Size exclusion chromatography (SEC) and intrinsic viscosity (η) measurements confirm the polymer's cyclic topology.



■ INTRODUCTION

The surface, thermodynamic, photophysical, and solution properties of cyclic polymers are different from those of their linear analogues. On surfaces, cyclic polymers exhibit lower friction,[1−3] antifouling capability,[3] modified surface-polymer concentrations,[4] smaller nanostructured domain spacing,[5] and improved dewetting kinetics during surface annealing.[6] Higher T_g[7] values for cyclic polymers are a thermodynamic hallmark of their topology. Other thermodynamic differences include higher entanglement molecular weights[8] and increased crystallization rates and nucleation density.[9] Increased conjugation lengths for cyclic polymers also lead to clear differences in photophysical properties including enhanced fluorescence,[10] excited-state lifetimes,[10] and a higher refractive index.[11,12] Showing promise in medical applications for drug delivery,[13−15] in solution,[16] cyclic polymers exhibit lower intrinsic viscosities,[17,18] prevent nanoparticle aggregation, and have elevated micelle cloud point temperatures,[19] resulting in prolonged blood circulation.[13,20]

Exploiting the favorable properties of cyclic polymers requires significant advances in synthetic methodologies and, in particular, catalyst design. Appearing rapidly in the literature are major breakthroughs in catalysts for ring expansion metathesis polymerization (REMP).[21−26] The critical design feature involves tethering a metal−carbon double bond, or in one case, a metallacyclobutane,[24] to the metal center through ligand design. Cyclic alkenes, most commonly norbornene,[21,22,24,26] undergo ring expansion with tethered metal−carbon double bonds to give cyclic polymers. REMP of cyclic alkenes provides pure cyclic polymers[27] in high yields,[21,22] stereoregular derivatives,[21] bottlebrush derivatives,[28,29] gels,[28,30] and cross-linked networks.[30] In this report, we expand on the concept of ring expansion and introduce for the first time a catalyst bearing a *tethered alkylidyne* capable of polymerizing cyclic alkynes to produce high-molecular-weight ethynylene-linked cyclic polymers.

Figure 1 depicts a prototype catalyst design and a proposed ring expansion alkyne metathesis polymerization (REAMP) mechanism. The synthetic approach is to replace an ancillary ligand with a chelate capable of binding to the metal ion through both X-type and alkylidyne coordination. The proposed mechanism involves (1) initial cycloaddition of a cyclic alkyne to the tethered alkylidyne, (2) subsequent ring opening, (3) propagation via consecutive cycloadditions and ring-opening to expand the ring, and (4) intramolecular metathesis with any of the internal alkynes to release the ethynylene-linked cyclic polymer.

A tethered alkylidyne is a prerequisite to execute REAMP and to access these cyclic polymers on a large scale with controllable syntheses. An obvious challenge is the linear nature of the metal−carbon triple bond. Required is a ligand design that can overcome the 180° angle and yet tether back to the metal ion. Overcoming these challenges, herein we present the synthesis of a tethered W-alkylidyne and demonstrate REAMP for the first time.

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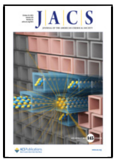

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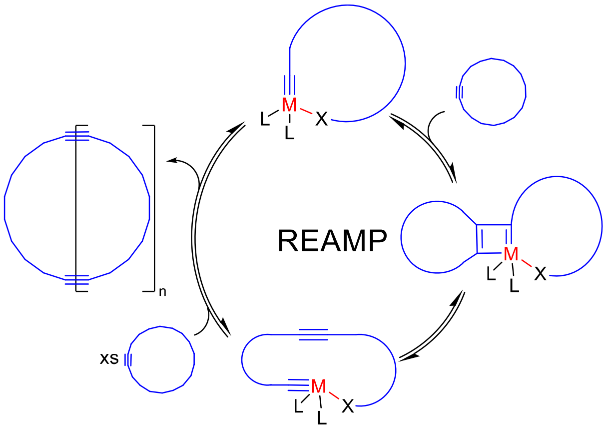


Figure 1. Proposed REAMP mechanism featuring a tethered alkylidyne as the initiator. For simplicity, the original tether is depicted to reform after intramolecular metathesis yielding a cyclic polymer.

RESULTS AND DISCUSSION

The strategy for synthesizing a tethered alkylidyne involves attaching an yne-ol proligand via simultaneous alcoholysis and alkyne metathesis with a preformed alkylidyne complex. The proligand synthesis begins with the incomplete bromination[31] of (*o*-(hydroxymethyl)phenyl)methanol (**1**) to give (2-(bromomethyl)phenyl)methanol (**2**). Combining **2** with a propargyl Grignard[32] attaches the TMS-protected alkyne to yield **3**. Removing the TMS group followed by Sonogashira coupling with iodobenzene provides the final yne-ol proligand **5** (Scheme 1).[33]

Scheme 2 depicts the synthesis of tethered alkylidyne **7**. Remarkably, the synthesis of **7** is relatively straightforward and proceeds with the desired combination of alcoholysis and metathesis. Simply combining complex **6**[34] with proligand **5** produces the symmetric bimetallic tethered alkylidyne complex **7** as a pale-yellow solid in 71% yield. Conducting the reaction in a sealable NMR tube in C_6D_6 allows the reaction progress to be monitored. A ^{1}H NMR spectrum of the reaction mixture reveals signals attributable to 2,6-diisopropylphenol and (3,3-dimethylbut-1-yn-1-yl)benzene, indicating successful alcoholysis and metathesis.

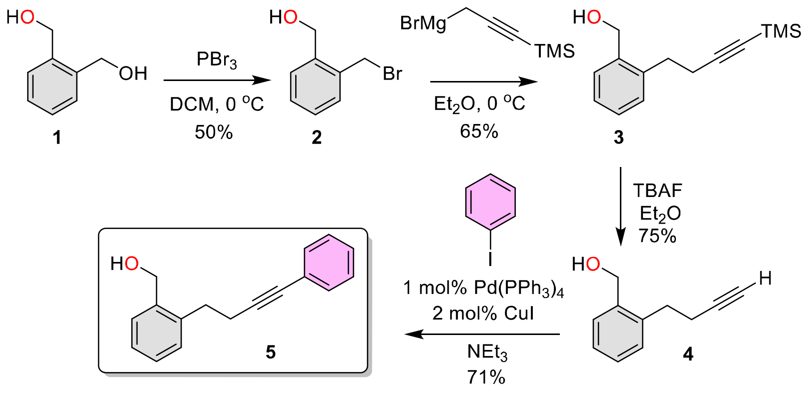
Yellow crystals deposit from a saturated solution of **7** in benzene/pentane (1:8). Figure 2 depicts the truncated molecular structure of **7** derived from single-crystal X-ray data. Modeling extensive disorder throughout the complex due to multiple ligand conformations and solvent inclusions provides satisfactory data refinement. Confirmed from the data are the presence of a tethered alkylidyne functionality and that complex **7** is a dimer. Reported in the literature are several alkoxide-bridged dimers of alkylidynes.[35−39] Thus, it is unsurprising that the dimer binds through the relatively small bridging alkoxides in the tether. With a separation of ∼3.55 Å, the W···W distance is large enough to discount any metal···metal bonding.[37,40] Consistent with literature values to be considered an alkylidyne, the W≡C bond is ∼1.786(5) Å.[41−45] Finally, suggesting some strain within the tethered linkage, the ∠W≡C−C of 168.7(4)° clearly deviates from 180°.

The ^{1}H NMR spectrum of *isolated* crystals of **7** exhibits signals consistent with the multiple ligand conformers that complicate the X-ray data. The spectrum contains signals involving at least three conformers. Comparing signal intensities for the neopentyl methyl protons, the conformational isomers are in a 40:6:3 ratio.

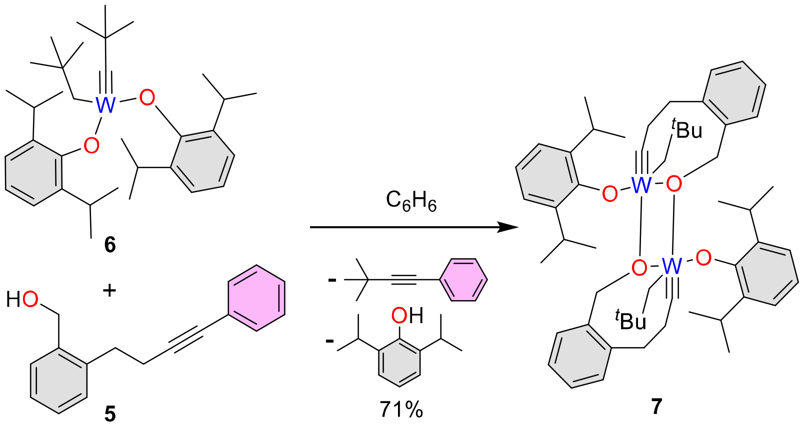
^{1}H, gHSQC, and gHMBC NMR experiments permit the assignment of NMR signals for the dominant isomer (see Supporting Information for atom labeling and full assignment). Heteronuclear 2-D NMR experiments confirm the nature of the carbon−tungsten bonds. The resonance corresponding to the alkylidyne carbon appears at 286.5 ppm, whereas the alkyl M−C bond resonates at 85.9 ppm, both within the expected regions for carbon atoms bonded to tungsten via triple and single bonds.[46] 1-D NOESY/EXSY experiments confirm that the conformers rapidly isomerize in solution. Irradiation of the neopentyl signal at 1.01 ppm (in toluene-d_8) results in signal inversions at 1.59 and 1.53 ppm. The inverted signals indicate that all of the conformers are in dynamic exchange (see Supporting Information Figures S13 and S14).

Tungsten alkylidyne dimers formed through bridging alkoxides reported in the literature can dissociate in solution.[39,42] However, complex **7** and each of its conformational isomers retain their dimer compositions in solution. A 2-D DOSY spectrum reveals that all of the conformers have the same diffusion coefficient expected for a dimer (see Supporting Information S15). Strongly coordinating substrates break apart tungsten alkylidyne dimers.[35,38] Adding excess pyridine to a sealable NMR tube resulted in spectra consistent with pyridine coordination to form a monomer. Interestingly, the pyridine coordination is reversible. All the NMR signals attributable to

Scheme 1. Synthesis of Yne-ol Proligand 5



Scheme 2. Synthesis of Tethered Alkylidyne Dimer 7



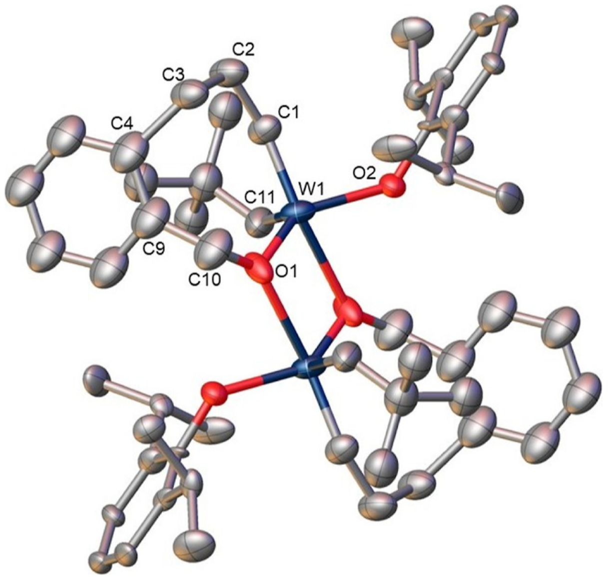


Figure 2. Molecular structure of complex 7. Solvent and disordered parts and hydrogen atoms are removed for clarity.

dimer 7 reappear upon removing pyridine in vacuo (see Supporting Information, S16).

REAMP requires a cyclic alkyne monomer. Ethynylene-linked cyclic polymers are rare and typically comprise oligomers with approximately 20 monomer units or less.[47−49] In one case,[50] intramolecular backbiting during ring opening alkyne metathesis (ROAMP) of 5,6,11,12-tetradehydrobenzo-[*a*,*e*][8]annulene (**8**) using EtC≡Mo[OC(CH_3)(CF_3)$_2$]$_3$dme as the initiator yields rings and some linear polymers. Catalyst 7 polymerizes **8** to give high-molecular-weight ethynylene-linked cyclic polymers for the first time (Scheme 3).[51]

Scheme 3. REAMP of Strained Cycloalkyne 8 Using Catalyst 7

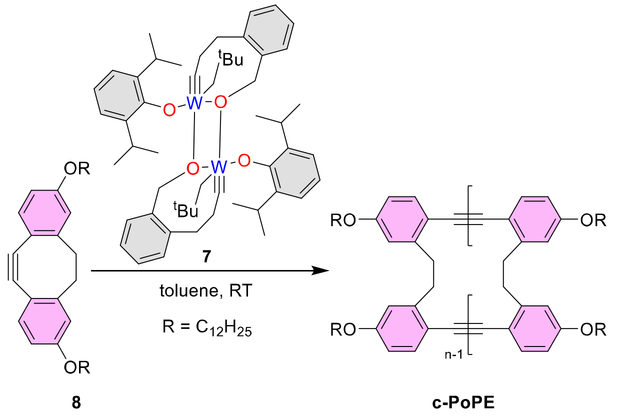


Table 1. Catalysis Conditions and Characterization Data for the Synthesis of Linear and Cyclic Polymers[d]

entry	time[a]	M_n[b]	Đ[b]	yield %[c]
c-PoPE-5	5	122,000	9.03	70
c-PoPE-10	10	198,000	4.42	80
c-PoPE-15	15	260,000	5.20	79
c-PoPE-25	25	280,000	4.29	80
l-PoPE	5	148,000	3.10	89

[a] Minutes. [b] Determined (g/mol) by size-exclusion chromatography (SEC) using dichlorobenzene (DCB) as the mobile phase at 140 °C. [c] Isolated yield. [d] Conducting the polymerization at 50 °C results in a material that is insoluble.

NMR spectroscopic interrogation (25 °C) of a sealable NMR tube (C_6D_6) charged with complex 7, and 25 equiv of **8** revealed signals attributable to successful polymer synthesis. Evident after 1.5 h is the complete consumption of the monomer and the formation of a white precipitate consisting of cyclic poly-(*o*-phenylene ethynylene) (**c-PoPE**). ^{1}H NMR analysis of the isolated polymer in $CDCl_3$ at 47 °C matches literature values for the linear polymer, including the appearance of one singlet at 3.21 ppm for the ethyl bridge protons. Using catalyst 7 in toluene with a 50:1 monomer to catalyst M≡C bond ratio and quenched at 5, 10, 15, and 25 min, a series of polymer samples were generated. Table 1 lists the conditions and polymer characterization data. Conducted using a separately prepared batch of catalyst 7, a second independent set of polymerizations was executed (see Supporting Information). All of the polymerizations result in highly viscous solutions and polymeric materials that are poorly soluble, making analysis challenging. However, high-temperature SEC experiments, light scattering, and intrinsic viscosity measurements provide data that support a cyclic topology for the polymers. Clear from the data is that the polymers formed via REAMP are of high molecular weight with a degree of polymerization ranging between 200 and 480. The high dispersities (Đ) are a consequence of the following:

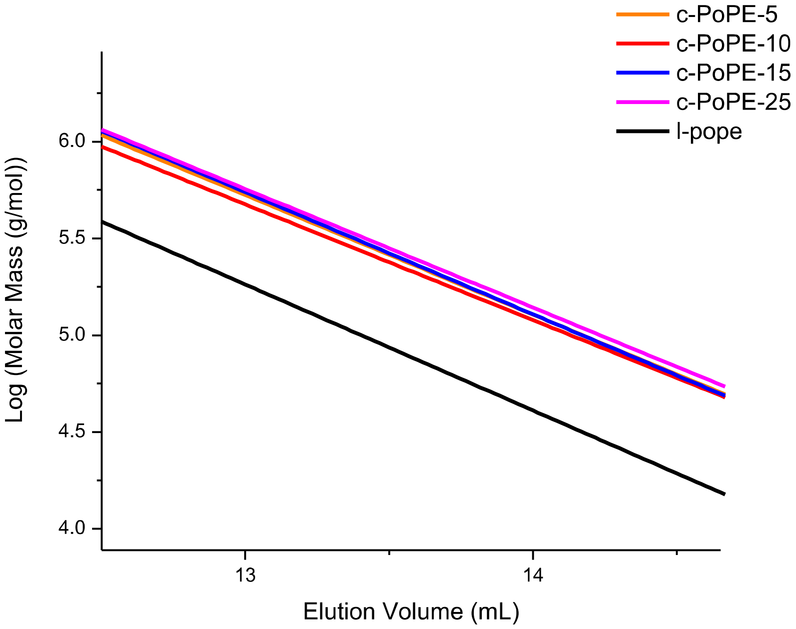


Figure 3. Log (molar mass) versus elution volume for cyclic and linear **PoPE** samples.

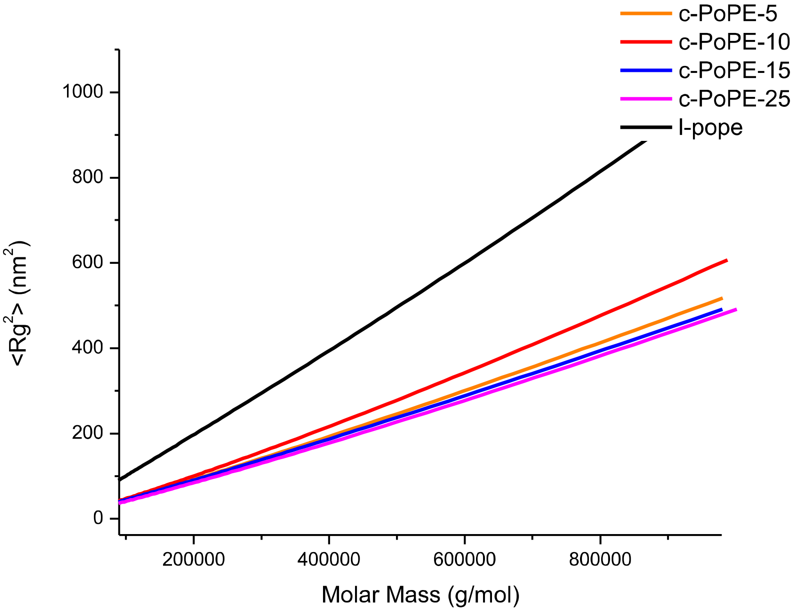


Figure 4. Plot of $\langle R_g^2 \rangle$ versus molar mass of cyclic and linear **PoPE** samples.

(1) rapid increase in viscosity upon polymer formation, (2) precipitation of polymer during polymerization, (3) potential for multiple active sites due to the dinuclear nature of the catalyst, and (4) access to multiple catalyst conformers (X-ray/NMR) that have different rates of initiation and/or propagation.

Evidence of a cyclic topology comes from various measurements that examine the hydrodynamic volume of the polymers and their intrinsic viscosities. The tungsten alkylidyne $(O^tBu)_3W{\equiv}C^tBu$ is active for the polymerization of **8** to give linear poly(*o*-phenylene ethynylene) (**l-PoPE**), thus providing a direct comparison of any potential differences due to topology.[51] Cyclic polymers with the same molar mass elute later than their linear counterparts due to their smaller hydrodynamic volume.[52−54] Figure 3 depicts a plot of the log of molecular weight versus elution volume for cyclic (**c-PoPE-5, 10, 15, and 25**) and linear (**l-PoPE**) polymers. Polymers synthesized via REAMP catalyst **7** elute later than the linear polymers, which is a hallmark of a cyclic topology.

Another property difference between cyclic and linear polymers is the mean square radius, $\langle R_g^2 \rangle$. Figure 4 depicts the $\langle R_g^2 \rangle$ versus log molar mass of **l-PoPE** versus the **c-PoPE** samples. The mean square radius of **l-PoPE** increases as a function of molecular weight at a greater rate than for the cyclic polymer samples. As the molecular weight increases, the linear analogue will grow outward more rapidly than the more compact cyclic polymers. Using **c-PoPE-15** for example, the data reveal a ratio of $\langle R_g^2 \rangle_{\text{cyclic}}/\langle R_g^2 \rangle_{\text{linear}}$ of 0.469 ± 0.100

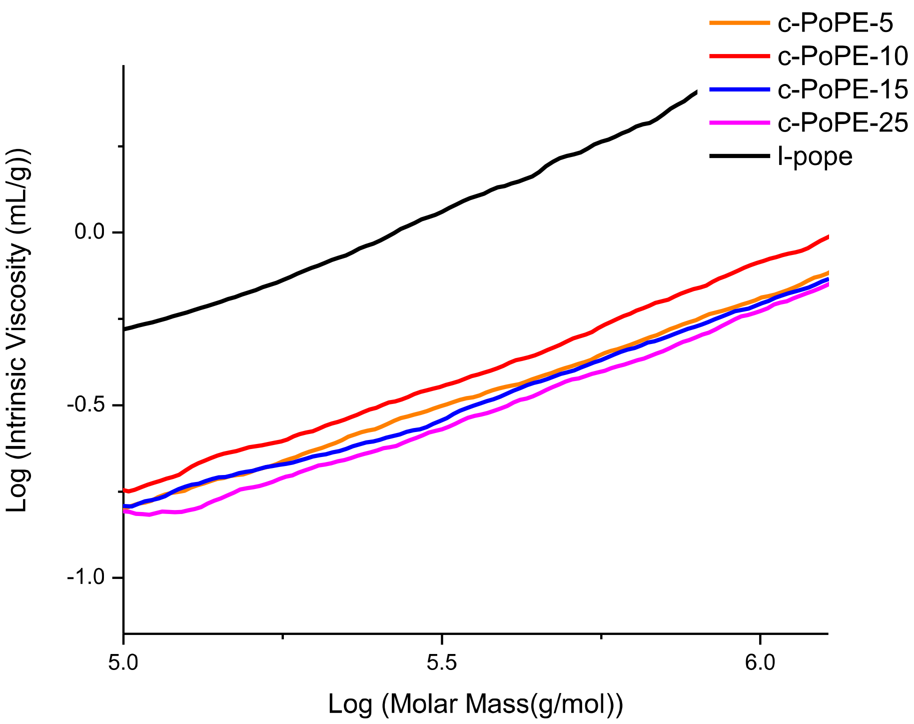


Figure 5. Mark–Houwink–Sakurada plot of cyclic and linear **PoPE** samples.

across a molecular weight range of 200 to 600 kDa. The theoretical ratio is 0.5.[55]

Confirmation of a cyclic topology also comes from a demonstration of lower intrinsic viscosities [η] of cyclic versus linear polymers via a Mark–Houwink–Sakurada (MHS) plot. Recent prediction of the expected ratio of $[\eta]_{\text{cyclic}}/[\eta]_{\text{linear}}$ in a good solvent is 0.58 ± 0.01.[56] However, experimental data vary broadly.[6,21,22,54,57,58] Figure 5 depicts [η] versus log molar mass for the linear and cyclic **PoPE** samples and clearly demonstrates the topological difference. At a given molecular weight, a solution of cyclic polymer is denser than that of its linear analogue. A well-solvated linear molecule will disrupt the laminar flow of the solution to a greater extent than a cyclic molecule of the same molecular weight. The MHS plots reveal numerical *a*-values of 0.7, indicating that both cyclic (**c-PoPE-5, 10, 15, 25**) and linear (**l-PoPE**) polymers exhibit a similar conformation in solution.

CONCLUSIONS

Demonstrated for the first time is the synthesis of tethered W-alkylidyne complex **7** via simultaneous alcoholysis and metathesis of an yne-ol proligand **5** with an alkylidyne complex. The tethered alkylidyne **7** has the requisite ring strain to open cyclic alkynes and produces cyclic polymers, thus expanding the reach of alkyne metathesis applications.[59,60] This ring opening activity paired with the growing tether allows the generation of high-molecular-weight cyclic polyalkynes via REAMP. It is reasonable to expect that many other tethered alkylidynes will now be accessible using the strategy of combining an appropriate yne-ol proligand with an alkylidyne, thus expanding access to high-molecular-weight cycloparaphenylacetylenes[61,62] (CPPAs) and other cyclic poly(aryleneethynylene)s (PAEs)[48,49,63,64] via REAMP.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jacs.3c08717.

> Discussions of experimental details, ^{1}H, ^{13}C{^{1}H} chemical shift assignments, and schematic molecular structures; NMR spectra; gHSQC and gHMBC spectra; NOESY spectra; 2D DOSY spectra; SEC traces; log of molar mass versus elution volume plot; mean squared radius of gyration versus molecular weight plot; and intrinsic viscosity versus molecular weight plot (PDF)

Accession Codes

CCDC 2271178 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript. A.M.B. and J.C. contributed equally to this paper.

Notes

The authors declare the following competing financial interest(s): University of Florida, A.S.V., and A.M.B. have filed patents related to this work.

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■ REFERENCES

(1) Patel, A.; Cosgrove, T.; Semlyen, J. A. Studies of Cyclic and Linear Poly(Dimethylsiloxanes): 30. Adsorption Studies on Silica in Solution. *Polymer* **1991**, *32*, 1313−1317.

(2) Verbraeken, B.; Hoogenboom, R. Cyclic Polymers: From Scientific Curiosity to Advanced Materials for Gene Delivery and Surface Modification. *Angew. Chem., Int. Ed.* **2017**, *56*, 7034−7036.

(3) Morgese, G.; Trachsel, L.; Romio, M.; Divandari, M.; Ramakrishna, S. N.; Benetti, E. M. Topological Polymer Chemistry Enters Surface Science: Linear versus Cyclic Polymer Brushes. *Angew. Chem., Int. Ed.* **2016**, *55*, 15583−15588.

(4) Gaitho, F. M.; Tsige, M.; Mola, G. T.; Pellicane, G. Surface Segregation of Cyclic Chains in Binary Melts of Thin Polymer Films: The Influence of Constituent Concentration. *Polymers* **2018**, *10*, 324.

(5) Goodson, A. D.; Troxler, J. E.; Rick, M. S.; Ashbaugh, H. S.; Albert, J. N. L. Impact of Cyclic Block Copolymer Chain Architecture and Degree of Polymerization on Nanoscale Domain Spacing: A Simulation and Scaling Theory Analysis. *Macromolecules* **2019**, *52*, 9389−9397.

(6) Wang, L.; Xu, L.; Liu, B.; Shi, T.; Jiang, S.; An, L. The Influence of Polymer Architectures on the Dewetting Behavior of Thin Polymer Films: From Linear Chains to Ring Chains. *Soft Matter* **2017**, *13*, 3091−3098.

(7) Clarson, S. J.; Dodgson, K.; Semlyen, J. A. Studies of Cyclic and Linear Poly(Dimethylsiloxanes): 19. Glass Transition Temperatures and Crystallization Behaviour. *Polymer* **1985**, *26*, 930−934.

(8) Niu, W.; Gonsales, S. A.; Kubo, T.; Bentz, K. C.; Pal, D.; Savin, D. A.; Sumerlin, B. S.; Veige, A. S. Polypropylene: Now Available without Chain Ends. *Chem* **2019**, *5*, 237−244.

(9) Zaldua, N.; Liénard, R.; Josse, T.; Zubitur, M.; Mugica, A.; Iturrospe, A.; Arbe, A.; De Winter, J.; Coulembier, O.; Müller, A. J. Influence of Chain Topology (Cyclic versus Linear) on the Nucleation and Isothermal Crystallization of Poly(l -Lactide) and Poly(d -Lactide). *Macromolecules* **2018**, *51*, 1718−1732.

(10) Zhu, X.; Zhou, N.; Zhang, Z.; Sun, B.; Yang, Y.; Zhu, J.; Zhu, X. Cyclic Polymers with Pendent Carbazole Units: Enhanced Fluorescence and Redox Behavior. *Angew. Chem., Int. Ed.* **2011**, *50*, 6615−6618.

(11) Orrah, D. J.; Semlyen, J. A.; Ross-Murphy, S. B. Studies of Cyclic and Linear Poly(Dimethylsiloxanes): 28. Viscosities and Densities of Ring and Chain Poly(Dimethylsiloxane) Blends. *Polymer* **1988**, *29*, 1455−1458.

(12) Bannister, D. J.; Semlyen, J. A. Studies of Cyclic and Linear Poly(Dimethyl Siloxanes): 6. Effect of Heat. *Polymer* **1981**, *22*, 377−381.

(13) Chen, B.; Jerger, K.; Fréchet, J. M.; Szoka, F. C. The Influence of Polymer Topology on Pharmacokinetics: Differences between Cyclic and Linear PEGylated Poly(Acrylic Acid) Comb Polymers. *J. Controlled Release* **2009**, *140*, 203−209.

(14) Golba, B.; Benetti, E. M.; De Geest, B. G. Biomaterials Applications of Cyclic Polymers. *Biomaterials* **2021**, *267*, 120468.

(15) Pal, D.; Garrison, J. B.; Miao, Z.; Diodati, L. E.; Veige, A. S.; Sumerlin, B. S. Nanobowls from Amphiphilic Core-Shell Cyclic Bottlebrush Polymers. *Macromolecules* **2022**, *55*, 7446−7453.

(16) Miao, Z.; Kubo, T.; Pal, D.; Sumerlin, B. S.; Veige, A. S. pH-Responsive Water-Soluble Cyclic Polymer. *Macromolecules* **2019**, *52*, 6260−6265.

(17) Jeong, Y.; Jin, Y.; Chang, T.; Uhlik, F.; Roovers, J. Intrinsic Viscosity of Cyclic Polystyrene. *Macromolecules* **2017**, *50*, 7770−7776.

(18) Liénard, R.; De Winter, J.; Coulembier, O. Cyclic polymers: Advances in their Synthesis, Properties, and Biomedical Applications. *J. Polym. Sci.* **2020**, *58*, 1481−1502.

(19) Honda, S.; Yamamoto, T.; Tezuka, Y. Topology-Directed Control on Thermal Stability: Micelles Formed from Linear and Cyclized Amphiphilic Block Copolymers. *J. Am. Chem. Soc.* **2010**, *132*, 10251−10253.

(20) Nasongkla, N.; Chen, B.; Macaraeg, N.; Fox, M. E.; Fréchet, J. M. J.; Szoka, F. C. Dependence of Pharmacokinetics and Biodistribution on Polymer Architecture: Effect of Cyclic versus Linear Polymers. *J. Am. Chem. Soc.* **2009**, *131*, 3842−3843.

(21) Gonsales, S. A.; Kubo, T.; Flint, M. K.; Abboud, K. A.; Sumerlin, B. S.; Veige, A. S. Highly Tactic Cyclic Polynorbornene: Stereoselective Ring Expansion Metathesis Polymerization of Norbornene Catalyzed by a New Tethered Tungsten-Alkylidene Catalyst. *J. Am. Chem. Soc.* **2016**, *138*, 4996−4999.

(22) Nadif, S. S.; Kubo, T.; Gonsales, S. A.; VenkatRamani, S.; Ghiviriga, I.; Sumerlin, B. S.; Veige, A. S. Introducing "Ynene" Metathesis: Ring-Expansion Metathesis Polymerization Leads to Highly Cis and Syndiotactic Cyclic Polymers of Norbornene. *J. Am. Chem. Soc.* **2016**, *138*, 6408−6411.

(23) Jakhar, V.; Pal, D.; Ghiviriga, I.; Abboud, K. A.; Lester, D. W.; Sumerlin, B. S.; Veige, A. S. Tethered Tungsten-Alkylidenes for the Synthesis of Cyclic Polynorbornene via Ring Expansion Metathesis: Unprecedented Stereoselectivity and Trapping of Key Catalytic Intermediates. *J. Am. Chem. Soc.* **2021**, *143*, 1235−1246.

(24) Mandal, U.; Ghiviriga, I.; Abboud, K. A.; Lester, D. W.; Veige, A. S. Double Tethered Metallacyclobutane Catalyst for Cyclic Polymer Synthesis. *J. Am. Chem. Soc.* **2021**, *143*, 17276−17283.

(25) Edwards, J. P.; Wolf, W. J.; Grubbs, R. H. The Synthesis of Cyclic Polymers by Olefin Metathesis: Achievements and Challenges. *J. Polym. Sci., Part A: Polym. Chem.* **2019**, *57*, 228−242.

(26) Wang, T. W.; Huang, P. R.; Chow, J. L.; Kaminsky, W.; Golder, M. R. A Cyclic Ruthenium Benzylidene Initiator Platform Enhances Reactivity for Ring-Expansion Metathesis Polymerization. *J. Am. Chem. Soc.* **2021**, *143*, 7314−7319.

(27) Bielawski, C. W.; Benitez, D.; Grubbs, R. H. Synthesis of Cyclic Polybutadiene via Ring-Opening Metathesis Polymerization: The Importance of Removing Trace Linear Contaminants. *J. Am. Chem. Soc.* **2003**, *125*, 8424−8425.

(28) Zhang, K.; Lackey, M. A.; Wu, Y.; Tew, G. N. Universal Cyclic Polymer Templates. *J. Am. Chem. Soc.* **2011**, *133*, 6906−6909.

(29) Xia, Y.; Boydston, A. J.; Grubbs, R. H. Synthesis and Direct Imaging of Ultrahigh Molecular Weight Cyclic Brush Polymers. *Angew. Chem., Int. Ed.* **2011**, *50*, 5882−5885.

(30) Zhang, K.; Lackey, M. A.; Cui, J.; Tew, G. N. Gels Based on Cyclic Polymers. *J. Am. Chem. Soc.* **2011**, *133*, 4140−4148.

(31) Doyle, M. P.; Chapman, B. J.; Hu, W.; Peterson, C. S.; McKervey, M. A.; Garcia, C. F. Catalytic Intramolecular Addition of Metal Carbenes to Remote Furans. *Org. Lett.* **1999**, *1*, 1327−1329.

(32) Acharya, H. P.; Miyoshi, K.; Kobayashi, Y. Mercury-Free Preparation and Selective Reactions of Propargyl (and Propargylic) Grignard Reagents. *Org. Lett.* **2007**, *9*, 3535−3538.

(33) Patil, N. T.; Lutete, L. M.; Wu, H.; Pahadi, N. K.; Gridnev, I. D.; Yamamoto, Y. Palladium-Catalyzed Intramolecular Asymmetric Hydroamination, Hydroalkoxylation, and Hydrocarbonation of Alkynes. *J. Org. Chem.* **2006**, *71*, 4270−4279.

(34) Tonzetich, Z. J.; Lam, Y. C.; Müller, P.; Schrock, R. R. Facile Synthesis of a Tungsten Alkylidyne Catalyst for Alkyne Metathesis. *Organometallics* **2007**, *26*, 475−477.

(35) Chisholm, M. H.; Eichhorn, B. W.; Folting, K.; Huffman, J. C. Tungsten—Carbon, Carbon—Hydrogen, and Carbon—Carbon Bond Activation in the Chemistry of $1,2\text{-}W_2R_2(OR')4(WW)$ Complexes. 1. Alkyne-Promoted Metal-to-Metal Alkyl Migrations, W = W/C = C Bond Metathesis, and Metallacyclopropene Formation. *Organometallics* **1989**, *8*, 49−66.

(36) Dembinski, R.; Szafert, S.; Haquette, P.; Lis, T.; Gladysz, J. A. A New Route to Heterobimetallic C3 Complexes via C≡C Metatheses of 1,3-Diynyl Ligands: Synthesis and Structure of $(H_5\text{-}C_5Me_5)Re(NO)(PPh_3)(C{\equiv}CC{\equiv})W(O\text{-}t\text{-}Bu)_3$. *Organometallics* **1999**, *18*, 5438−5440.

(37) Chisholm, M. H.; Conroy, B. K.; Huffman, J. C. Competitive Carbon-Carbon Bond Formation and Cleavage and Cluster Formation in the Reaction between 3-Hexyne and Hexaisopropoxytungsten. *Organometallics* **1986**, *5*, 2384−2386.

(38) Chisholm, M. H.; Hoffman, D. M.; Huffman, J. C. Isoelectronic Molecules with Triple Bonds to Metal Atoms (M = Mo, W): Crystal and Molecular Structures of Tri- Tert-Butoxytungsten Ethylidyne and Nitride. *Inorg. Chem.* **1983**, *22*, 2903−2906.

(39) Chisholm, M. H.; Huffman, J. C.; Marchant, N. L. Reactions of M-M Triple Bonds with C-N Triple Bonds: Adduct Formation (M = Mo) and Metathesis (M = W) as Seen in the Reactions Between Dimethylcyanamide and Hexaalkoxides of Dimolybdenum and Ditungsten. *J. Am. Chem. Soc.* **1983**, *105*, 6162−6163.

(40) Redshaw, C.; Humphrey, S. M. Complexes of Tungsten(IV,VI) Derived from Linked Aryloxide Ligands. *Polyhedron* **2006**, *25*, 1946−1954.

(41) VenkatRamani, S.; Huff, N. B.; Jan, M. T.; Ghiviriga, I.; Abboud, K. A.; Veige, A. S. New Alkylidyne Complexes Featuring a Flexible Trianionic ONO^{3-} Pincer-Type Ligand: Inorganic Enamine Effect versus Sterics in Electrophilic Additions. *Organometallics* **2015**, *34*, 2841−2848.

(42) Churchill, M. R.; Youngs, W. J. Crystal Structure and Molecular Geometry of $W({\equiv}CCMe_3)({=}CHCMe_3)(CH_2CMe_3)(dmpe)$, a Mononuclear Tungsten(VI) Complex with Metal-Alkylidyne, Metal-Alkylidene, and Metal-Alkyl Linkages. *Inorg. Chem.* **1979**, *18*, 2454−2458.

(43) Schrock, R. R. High-Oxidation-State Molybdenum and Tungsten Alkylidyne Complexes. *Acc. Chem. Res.* **1986**, *19*, 342−348.

(44) Sarkar, S.; McGowan, K. P.; Kuppuswamy, S.; Ghiviriga, I.; Abboud, K. A.; Veige, A. S. An OCO^{3-} Trianionic Pincer Tungsten(VI) Alkylidyne: Rational Design of a Highly Active Alkyne Polymerization Catalyst. *J. Am. Chem. Soc.* **2012**, *134*, 4509−4512.

(45) Venkatramani, S.; Ghiviriga, I.; Abboud, K. A.; Veige, A. S. A New ONO^{3-} Trianionic Pincer Ligand with Intermediate Flexibility and Its Tungsten Alkylidene and Alkylidyne Complexes. *Dalton Trans.* **2015**, *44*, 18475−18486.

(46) Gordon, C. P.; Raynaud, C.; Andersen, R. A.; Copéret, C.; Eisenstein, O. Carbon-13 NMR Chemical Shift: A Descriptor for Electronic Structure and Reactivity of Organometallic Compounds. *Acc. Chem. Res.* **2019**, *52*, 2278−2289.

(47) Yang, H.; Jin, Y.; Du, Y.; Zhang, W. Application of Alkyne Metathesis in Polymer Synthesis. *J. Mater. Chem. A* **2014**, *2*, 5986−5993.

(48) Zhang, W.; Moore, J. S. Reaction Pathways Leading to Arylene Ethynylene Macrocycles via Alkyne Metathesis. *J. Am. Chem. Soc.* **2005**, *127*, 11863−11870.

(49) Ortiz, M.; Yu, C.; Jin, Y.; Zhang, W. Poly(Aryleneethynylene)s: Properties, Applications and Synthesis Through Alkyne Metathesis. *Top. Curr. Chem.* **2017**, *375*, 73−96.

(50) Von Kugelgen, S.; Bellone, D. E.; Cloke, R. R.; Perkins, W. S.; Fischer, F. R. Initiator Control of Conjugated Polymer Topology in Ring-Opening Alkyne Metathesis Polymerization. *J. Am. Chem. Soc.* **2016**, *138*, 6234−6239.

(51) Fischer, F. R.; Nuckolls, C. Design of Living Ring-Opening Alkyne Metathesis. *Angew. Chem.* **2010**, *122*, 7415−7418.

(52) Xia, Y.; Boydston, A. J.; Yao, Y.; Kornfield, J. A.; Gorodetskaya, I. A.; Spiess, H. W.; Grubbs, R. H. Ring-Expansion Metathesis Polymerization: Catalyst-Dependent Polymerization Profiles. *J. Am. Chem. Soc.* **2009**, *131*, 2670−2677.

(53) Boydston, A. J.; Xia, Y.; Kornfield, J. A.; Gorodetskaya, I. A.; Grubbs, R. H. Cyclic Ruthenium-Alkylidene Catalysts for Ring-Expansion Metathesis Polymerization. *J. Am. Chem. Soc.* **2008**, *130*, 12775−12782.

(54) McKenna, G. B.; Hadziioannou, G.; Lutz, P.; Hild, G.; Strazielle, C.; Straupe, C.; Rempp, P.; Kovacs, A. J. Dilute Solution Characterization of Cyclic Polystyrene Molecules and Their Zero-Shear Viscosity in the Melt. *Macromolecules* **1987**, *20*, 498−512.

(55) Zimm, B. H.; Stockmayer, W. H. The Dimensions of Chain Molecules Containing Branches and Rings. *J. Chem. Phys.* **1949**, *17*, 1301−1314.

(56) Rubio, A. M.; Freire, J. J.; Bishop, M.; Clarke, J. H. R. Θ State, Transition Curves, and Conformational Properties of Cyclic Chains. *Macromolecules* **1995**, *28*, 2240−2246.

(57) Roovers, J. Dilute-Solution Properties of Ring Polystyrenes. *J. Polym. Sci., Part A-2* **1985**, *23*, 1117−1126.

(58) Bielawski, C. W.; Benitez, D.; Grubbs, R. H. An "Endless" Route to Cyclic Polymers. *Science* **2002**, *297*, 2041−2044.

(59) Huang, S.; Lei, Z.; Jin, Y.; Zhang, W. By-design Molecular Architectures via Alkyne Metathesis. *Chem. Sci.* **2021**, *12*, 9591−9606.

(60) Fürstner, A. The Ascent of Alkyne Metathesis to Strategy-Level Status. *J. Am. Chem. Soc.* **2021**, *143*, 15538−15555.

(61) Lee, S.; Chénard, E.; Gray, D. L.; Moore, J. S. Synthesis of Cycloparaphenyleneacetylene via Alkyne Metathesis: C_{70} Complexation and Copper-Free Triple Click Reaction. *J. Am. Chem. Soc.* **2016**, *138*, 13814−13817.

(62) Kawase, T.; Darabi, H. R.; Oda, M. Cyclic [6]- and [8]Paraphenylacetylenes. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 2664−2666.

(63) Bunz, U. H. Poly(aryleneethynylene)s: Synthesis, Properties, Structures, and Applications. *Chem. Rev.* **2000**, *100*, 1605−1644.

(64) Haque, A.; Al-Balushi, R. A.; Al-Busaidi, I. J.; Khan, M. S.; Raithby, P. R. Rise of Conjugated Poly-ynes and Poly(Metalla-ynes): From Design Through Synthesis to Structure-Property Relationships and Applications. *Chem. Rev.* **2018**, *118*, 8474−8597.