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Living Polymerization

Design of Living Ring-Opening Alkyne Metathesis[**]

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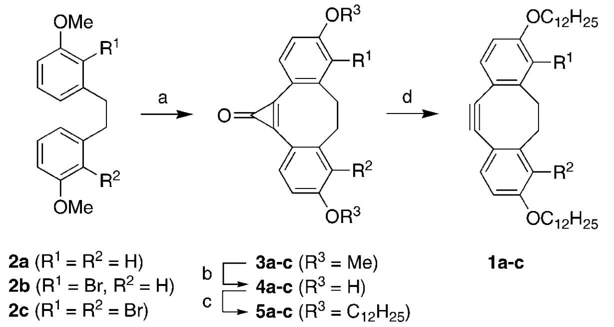
Despite the tremendous impact of alkene ring-opening metathesis polymerization (ROMP) on the design and the synthesis of polymers and functional materials,[1] examples for the analogous alkyne ROMP remain scarce.[2] This imbalance can be rationalized by the limited availability of commercially available catalysts[3] and the lack of alkyne metathesis monomers.[2] We present here the synthesis and a systematic study of the ROMP reactivity of an easily functionalized alkyne precursor derived from a ring-strained dibenzo[*a*,*e*]-[8]annulene. We find that both tungsten- and molybdenum-based catalysts yield high-molecular-weight polymers with alternating alkane and alkyne linkages along the poly(*ortho*-phenylene) backbone. A systematic study of different phenols and alcohols as the activating ligands in the trialkoxymolybdenum(VI) alkylidyne elucidates the design rules to create living alkyne ROMP.

Previously we found that the ROMP reaction of 5,6-didehydrodibenzo[*a*,*e*]cyclooctatetraene proceeds with Schrock's tungsten catalyst.[2d] Unfortunately this monomer cannot be easily derivatized because of its poor thermal and photochemical stability. The poor stability also leads to high polydispersity and a non-living polymeric system. To overcome this limitation we substituted the olefin bridge in the 5,6-didehydrodibenzo[*a*,*e*]cyclooctatetraene with a saturated ethyl linker, **1a–c** (Scheme 1). These strained alkynes (**1a–c**) can be conveniently synthesized on a multigram scale starting from the readily available 1,2-bis-(3-methoxyphenyl)ethanes **2a–c** as depicted in Scheme 1 (synthetic details are in the Supporting Information). Reaction of **2a–c** with tetrachlorocyclopropene and $AlCl_3$ yields the intermediate aromatic dichlorocyclopropenes that were hydrolyzed in situ to give the cyclopropenones **3a–c**. Cleavage of the methyl ethers and subsequent alkylation of the hydroxy groups in **4a–c** with solubilizing alkyl chains provides **5a–c**. Photochemical decarbonylation of the cyclopropenone[4a,b] produces the substituted [8]annulenes **1a–c** in 77–89 % yield. These monomers are far superior to other strained alkynes used in ROMP because they are indefinitely stable under ambient conditions and exposure to light.[5]



Scheme 1. Reaction conditions: a) $AlCl_3$, tetrachlorocyclopropene, CH_2Cl_2, −78 °C to 24 °C, 60–81 %; b) BBr_3, CH_2Cl_2, −78 °C, 99 %; c) NaH, $C_{12}H_{25}Br$, DMF, 24 °C, 51–63 %; d) THF/MeOH, *hν*, 24 °C, 77–89 %.

The structure of **1a–c** is consistent with its previously reported derivatives.[4] The ring strain stored in the compression of the triple bond angles from 180° to 155° (Figure 1) is

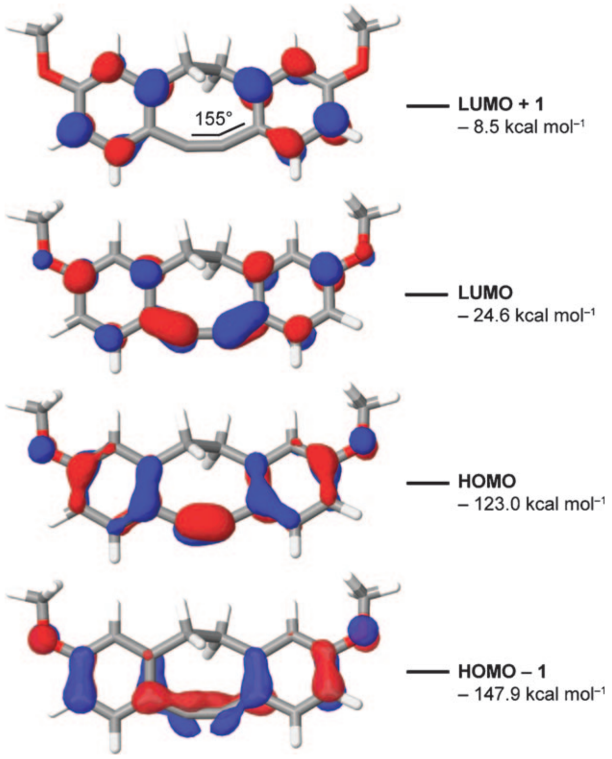


Figure 1. DFT B3LYP 6-311G** optimized structure of **1a**. Dodecyl chains are replaced by methyl groups to reduce computational complexity.

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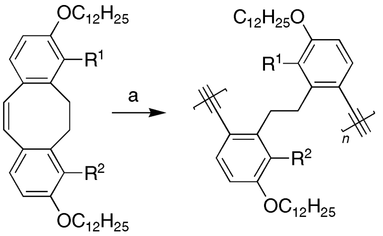
Supporting information for this article (synthesis of **1a–c**, DFT-optimized geometry of **1a**, ROMP, ^1H NMR, ^{13}C NMR of **6a–c**, and UV/Vis spectra of **1c** and **6c**) is available on the WWW under http://dx.doi.org/10.1002/anie.201003549.

reflected in a characteristic downfield shift ($\Delta\delta \approx 20$ ppm) of the alkyne carbon resonances in the ^{13}C NMR spectrum with respect to unstrained diphenylacetylene.

Figure 1 depicts the DFT (B3LYP 6-311G**) calculated frontier orbitals of **1a**.[6] The HOMO on the strained alkyne is localized in the π system conjugated to the adjacent phenyl rings. The π orbital distorted by the ring strain (HOMO−1) lies in the plane of the aromatic rings and is efficiently shielded by two neighboring protons. We conclude that an electron-deficient metathesis catalyst is likely to approach the strained alkyne perpendicular to the extended aromatic π system, thus activating the electronically as well as sterically most favorable π bond of the alkyne (HOMO).

We initially studied the alkyne ROMP of **1a–c** using the commercially available tungsten-based Schrock's metathesis catalyst. Adding [(tBuO)$_3$W≡CtBu] to a solution of **1a–c** in toluene at 24 °C leads to an instantaneous polymerization to give **6a–c** (Scheme 2) in essentially quantitative yields. The monomeric alkyne precursor is consumed within less than 10 s as judged by TLC and GC analysis of aliquots taken from the reaction mixture. Diagnostic for the ROMP reaction is the upfield shift of the NMR resonances of the acetylene ^{13}C atoms from ca. 110 ppm in **1a–c** to ca. 90 ppm in the polymers (Figures 2SI to 7SI). The polymerization is accompanied by a ca. 8 nm red-shift of the highest absorption peak in the UV/Vis spectrum (Figure 8SI).



1a-c **6a-c**

Scheme 2. Reaction conditions: a) [(tBuO)$_3$W≡CtBu], toluene, 24 °C, or [(N(tBu)Ar)$_3$Mo≡CCH$_2$CH$_3$] (Ar = 3,5-dimethylbenzene), alcohol/phenol, toluene, 24 °C.

Table 1 summarizes the GPC results obtained for the polymerization reactions of **1a–c** at various monomer/catalyst loadings. Since the polymers **6a–c** contain uncommon repeat units, only the relative M_n and PDI could be determined and are calibrated to polystyrene standards.[7] Polymer **6a** is insoluble in the reaction mixture, thus its molecular weight rarely exceeds 5.0×10^4, and a PDI greater than 2.0. The ROMP of the halogenated dibenzo[8]annulenes **1b** and **1c** shows a linear relationship between the monomer/catalyst (M/C) loading and the attained molecular weights. The polydispersity of **6b** and **6c** is also high, between 1.4 and 2.7. At equimolar amounts of monomer to catalyst, we observe by ^1H NMR spectroscopy that the monomer is consumed before all of the catalyst has initiated. Time-resolved GPC analysis reveals a fast initial linear phase ($t <$ 15 s) for the polymerization of the strained cyclooctyne leading to a polymer with low PDI (extrapolated to ca. 1.1) and high molecular weight (Figure 2). Our efforts to isolate this primary polymerization product have failed due to unpredictable variations in the initiation rates of individual catalyst batches. Once all starting material is consumed ($t >$ 15 s), residual uninitiated catalyst or terminal groups on the growing polymer are active enough to undergo competing cross-metathesis reactions with internal alkynes in the polymer backbone leading to a progressive broadening of the molecular weight distribution and an increased PDI. The low selectivity of Schrock's alkyne metathesis catalyst—ring-strained monomer over internal alkyne—led us to explore the ROMP activity of molybdenum-based catalyst systems.

Table 1: Number-average molecular weight (M_n) and polydispersity index (PDI) for **6a–c** at different monomer/catalyst (M/C) loadings.

Entry	Polymer[a]	M/C	M_n	PDI[b]
1	**6a**	10	54000	2.0
2	**6b**	10	65100	2.6
3	**6b**	5	19600	1.6
4	**6b**	2	13300	1.4
5	**6c**	10	32000	1.8
6	**6c**	5	19000	1.9
7	**6c**	2	15400	1.5

[a] Prepared by adding Schrock's tungsten catalyst [(tBuO)$_3$W≡CtBu] to a solution of **1a–c** in toluene at 24 °C. The polymer was precipitated with MeOH after 30 min. [b] PDI = M_n/M_w.

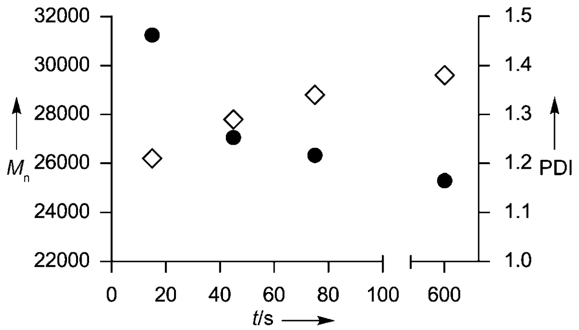


Figure 2. Time-resolved GPC data for the polymerization of **1c** with [(tBuO)$_3$W≡CtBu]. Samples were quenched at 15, 45, 75, and 600 s. M_n: ●; PDI: ◇.

Recent advances in alkyne metathesis catalyst design based on the formation of a trialkoxymolybdenum(VI) alkylidyne complex from readily available [(N-(tBu)Ar)$_3$Mo≡CCH$_2$CH$_3$] (Ar = 3,5-dimethylbenzene) and an activating alcohol/phenol give access to a variety of molecularly well-defined metathesis catalysts.[8] These systems have been extensively applied to acyclic diyne metathesis (ADIMET) and ring-closing-metathesis (RCM) reactions both in the synthesis of natural products and functional material systems.[9] The great majority of these reactions are run under dynamic equilibrium conditions, and are relatively unselective. The key requirement to prevent chain transfer and the resulting increase in the polydispersity is for the polymerization catalyst to discriminate between strained alkynes and unactivated triple bonds.

We screened 19 alkoxy and phenoxy ligands (ranging in pK_a from 4.7 to 18.6) in combination with the molybdenum propylidyne precursor [(*N*(*t*Bu)Ar)$_3$Mo≡CCH$_2$CH$_3$].[8] Table 2 summarizes the GPC characterization of the resulting polymers. All tested systems including the molybdenum precursor itself are active ROMP catalysts for **1c**. At a monomer/catalyst/ligand (M/C/L) loading of 5:1:3 the molecular weights range between 2.0×10^5 and 1.0×10^6. Ligands well known for their extraordinary performance in ADIMET and RCM reactions such as the fluorinated cresol (Table 2, entry 8),[8] the fluorinated phenols (entries 10–12),[10] and the fluorinated *tert*-butanols (entries 2, 17)[11] yield low-molecular-weight polymers ($M_n < 9.0\times10^4$) with PDIs exceeding 2.0. Catalyst systems that have previously been reported to fail in ADIMET and RCM reactions such as those in entries 18 and 20 give high-molecular-weight polymers.

Table 2: Number-average molecular weight (M_n) and polydispersity index (PDI) for **6c**.

Entry	Ligand[a]	pK_a[b]	M_n[d]	PDI[d]
1	2-NO$_2$-ArOH	4.7 (7.2)[12]	19 300	1.1
2	F$_6$-*t*BuOH	6.3	86 900	2.1
3	4-NO$_2$-ArOH	6.8 (7.2)[13]	1 020 000	1.8
4	3,5-(CF$_3$)$_2$-ArOH	7.6	170 000	1.3
5	3,5-F$_2$-ArOH	8.2	931 000	1.8
6	3-NO$_2$-ArOH	8.4 (8.4)[13]	248 000	1.3
7	2-CF$_3$-ArOH	8.4	599 000	1.4
8	4-CF$_3$-ArOH	8.6 (8.7)[13]	41 000	2.5
9	3-CF$_3$-ArOH	8.8 (8.9)[13]	917 000	2.0
10	2-F-ArOH	8.8 (8.7)[13]	73 400	2.3
11	3-F-ArOH	9.0 (9.2)[13]	30 400	2.9
12	4-F-ArOH	9.6 (9.9)[13]	90 700	2.5
13	2-naphthol	9.7 (9.5)[13]	52 400	2.1
14	phenol	9.9 (10.0)[14]	162 000	3.1
15	4-CH$_3$-ArOH	10.4 (10.3)[13]	71 800	2.0
16	4-CH$_3$O-ArOH	10.6 (10.1)[13]	62 700	2.1
17	F$_3$-*t*BuOH	11.5	56 800	2.1
18	*t*BuOH	16.0 (19.2)[13]	201 000	2.8
19	(+)-menthol	18.6	120 000	2.0
20	HN(*t*Bu)Ar	36.5[c]	153 000	1.7

[a] Substituted phenols are abbreviated as ArOH; HN(*t*Bu)Ar = *N-tert*-butyl-3,5-dimethylaniline. [b] pK_a values were calculated using the Schrödinger Jaguar software package[15] and are corrected for water (uncertainty ± 0.5) or [c] DMSO (uncertainty ± 1.4). Experimental values for water are given in brackets. [d] Polymer **6c** was prepared by adding a mixture of preformed metathesis catalyst (3:1 ligand/[(N(*t*Bu)Ar)$_3$Mo≡CCH$_2$CH$_3$]) to 5 parts of **1c** in toluene at 24 °C. The polymer was precipitated with MeOH after 150 s.

The best catalysts identified in this series were derived from 2- and 3-nitrophenol (entries 1, 6) or 3,5-bis(trifluoromethyl)phenol (entry 4) (PDI = 1.1, 1.3, and 1.3 respectively). Polymerizations performed in the presence of 2-nitrophenol yielded low-molecular-weight polymers indicating that the propagation reaction is slow relative to the catalyst initiation. All monomer is consumed in an initial linear ROMP phase ($t < 15$ s) (Figure 9SI) yielding a polymer of low polydispersity (PDI ≈ 1.1). Both the PDI as well as the M_n do not erode over time, thus the catalytic species formed is not capable of activating unstrained alkynes in the backbone of the growing polymer.

The catalytic groups at the end of the polymer chain remain active after the initial monomer has been consumed (Figure 3). Additional equivalents of **1c** added to the reaction mixture are readily incorporated into the growing polymer. GPC analysis of aliquots taken 40 s after each addition, show an incremental increase in molecular weight. The molecular weight distribution, however, remains essentially unaffected at a PDI of 1.1. We conclude from this data that the ROMP using the [(*N*(*t*Bu)Ar)$_3$Mo≡CCH$_2$CH$_3$]/2-nitrophenol catalyst system is living.

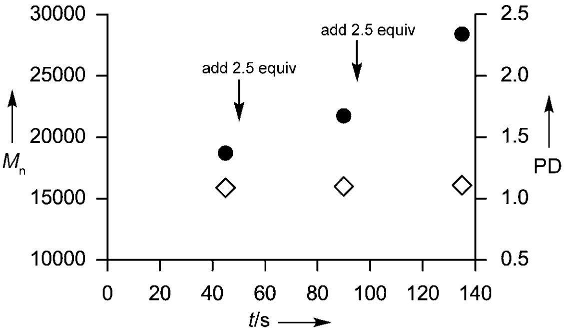


Figure 3. Time-resolved GPC data for the polymerization of **1c** with [(*N*(*t*Bu)Ar)$_3$Mo≡CCH$_2$CH$_3$] and 2-nitrophenol. Aliquots were quenched at 45, 90, and 135 s. 2×2.5 equivalents of **1c** were added at 50 and 90 s. M_n: ●; PDI: ◇.

Even though, the best ligand identified in this series features the lowest calculated pK_a (entry 1 in Table 2), we have been unsuccessful to establish a direct correlation between phenol/alcohol pK_a and the performance in polymerization reactions. Activating ligands commonly used in ADIMET and RCM reactions range in pK_a between 8–10 and yield consistently poor ROMP catalysts systems. We therefore encourage the search for potent ligands for alkyne ROMP at both extremes of the pK_a scale.

In summary, we have described the synthesis of highly functionalizable, strained, yet thermally stable cycloalkynes. These [8]annulenes readily undergo alkyne ROMP with tungsten- or molybdenum-based catalysts to yield soluble high-molecular-weight polymers with alternating alkane and alkyne linkages along the poly(*ortho*-phenylene) backbone. In a screening of activating ligands for the trialkoxymolybdenum(VI) alkylidyne complex we identified a catalyst system capable of discriminating between stained alkynes in the monomeric precursor and unactivated internal acetylenes in the growing polymer chain. A mixture of [(*N*(*t*Bu)Ar)$_3$Mo≡CCH$_2$CH$_3$] and 3 equivalents of 2-nitrophenol reliably yields living polymers with a PDI as low as 1.1. This catalyst system is the first example of a living alkyne ROMP reaction. This method yields functional polymers that serve as precursors to graphene ribbons and self-folding polymers.

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Keywords: alkynes · living polymerization · metathesis · ring-opening reactions · strained molecules

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[15] The calculated pK_a values correlate exceptionally well with the experiment. Significant deviations can only be observed at the extremes of the scale (Table 2, entries 1 and 18). Since the pK_a values of several phenols/alcohols are not reported in the literature, and the experimental method used in the determination varies for each entry we chose to rank the phenols/alcohols according to their calculated pK_a values.