Alkyne Polymers from Stable Butatriene Homologues: Controlled Radical Polymerization of Vinylidenecyclopropanes

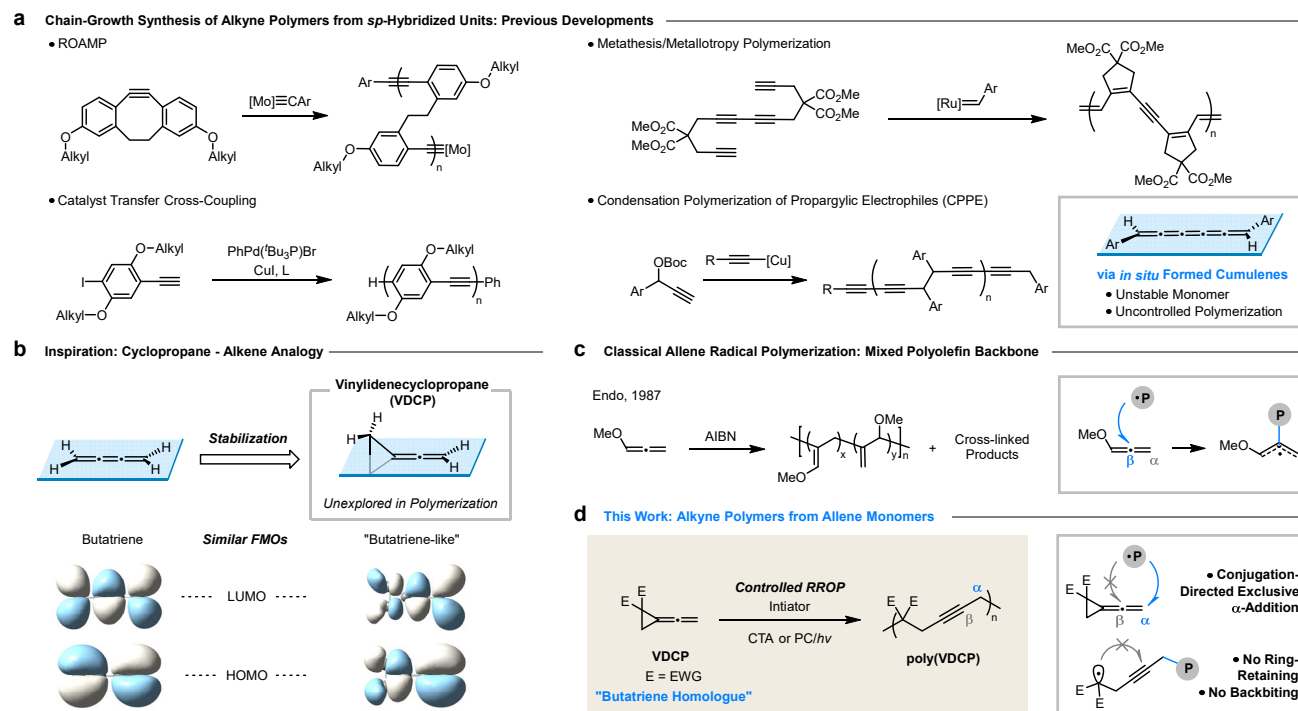Bin Wu, Qian-Jun Ding, Zheng-Lin Wang, and Rong Zhu*

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ABSTRACT Controlled polymerization of cumulenic monomers represents a promising yet underdeveloped strategy towards well-defined alkyne polymers. Here we report a stereoelectronic effect-inspired approach using simple vinylidenecyclopropanes (VDCPs) as butatriene homologues in controlled radical ring-opening polymerizations. While being thermally stable, VDCPs mimic butatrienes via conjugation of the cyclopropane ring. This leads to exclusive terminal-selective propagation that affords a highly structurally regular alkyne-based backbone, featuring complete ring-opening and no backbiting regardless of polymerization conditions.

Polymers with alkyne-based backbones have demonstrated interesting material properties and postpolymerization transformations.[1] Most methods to build alkyne polymers follow a step-growth mechanism that lacks precise control on molecular weights (MW) and end groups.[2] Hence, chain-growth methods have been pursued (Figure 1a). Prominent examples include ring-opening alkyne metathesis polymerization,[3] cascade metathesis/metallotropy polymerization,[4] and catalyst transfer Sonogashira polycondensation.[5] We recently disclosed the copper-catalyzed condensation polymerization of propargylic electrophiles (CPPE).[6] CPPE is distinct in using *in situ* formed [n]cumulenes (n = 3, 5) for a chain-growth process. However, controlled polymerization in this system is challenging partly due to the instability of cumulenes.[7]

The cyclopropane ring has long been known as a surrogate for C=C bonds.[8] In medicinal chemistry, a cyclopropyl moiety is often introduced as an alkene bioisostere for its higher metabolic stability.[9] Meanwhile, its electronic property closely resembles that of an alkene due to the π-overlap of the in-plane p orbitals. We thus became interested in adopting this concept in cumulenes (Figure 1b). Replacing the terminal C=C bond of butatriene by a cyclopropane ring leads to a strained allene, namely vinylidenecyclopropane (VDCP).[10] Despite of numerous studies, VDCP remains an unexplored monomer class in polymer chemistry, which is not surprising in the context that allene polymerization is largely complicated by regioselectivity issues except for few cases.[11] For example, Endo reported that alkoxyallenes underwent mixed 1,2- and 2,3-addition in radical polymerization (Figure 1c).[12] Nonetheless, we envisioned that VDCP could be a conceptually different allenic monomer because it is a "bent" butatrienes in a stereoelectronic sense, which can be inferred from its frontier orbitals. As a result, VDCP derivatives might react with an incoming electrophilic radical exclusively at the terminal carbon (α) like a butatriene, presumably also facilitated by the polarity effect.[13] Such a process, followed by ring opening to afford a nascent stabilized propagating radical, could lead to an alkyne-based main chain.

Figure 1. Background and design of VDCP as a butatriene homologue for controlled synthesis of alkyne polymers.

Here we report the first example of radical polymerization of allenes that produces an alkyne backbone (Figure 1d). Controlled radical ring-opening polymerization (RROP) of VDCPs was realized under reversible addition-fragmerization chain transfer (RAFT) and photoinduced-electron-transfer atom-transfer radical polymerization (PET-ATRP) conditions, respectively.[14] Poly(VDCP)s with high structural regularity were produced with good MW control and end group fidelity, which enabled block copolymer synthesis featuring a precise main-chain alkyne block segment. VDCPs underwent full ring-opening without any detectable backbiting regardless of concentration and temperature, under either uncontrolled or living polymerization conditions. This contrasts with classical vinyl-based monomers such as cyclic ketene acetals (CKA) and vinyl cyclopropanes (VCP), which might provide a unique cumulene-based angle for new ROP monomer design.[15]

We commenced our studies by analyzing the regiochemical outcome of the radical addition onto dimethyl 2-vinylidenecyclopropane-1,1-dicarboxylates (**M1**) (Figure 2a). Addition at the terminal methylene (α) would produce a vinyl radical **A**, followed by strain releasing β-scission to form homopropargylic radical **B**. Propagation would give the desired backbone. Such α-addition is consistent with a "butatriene-like" description of VDCP. However, competing addition at the central sp-hybridized carbon (β) could be driven by forming a stabilized allyl radical **C**, a regioselectivity that is frequently observed for allenes.[16]

Computation revealed that β-addition is indeed more thermodynamically favorable (**TS1**), however with a high barrier of 22.5 kcal/mol, while α-addition (**TS2**) is kinetically favored ($\Delta G^{\ddagger} = 16.4$ kcal/mol) (Figure 2b). The exothermic ring-opening process of the resulting vinyl radical **INT4** is essentially barrier

less (**TS3**), affording homopropargylic radical **INT5**, which can participate in the next propagation cycle. This result highlights the unique "butatriene-like" reactivity of VDCP due to conjugation of the cyclopropane ring. In addition, we calculated the 4-endo-dig backbiting process and found it highly unlikely (**TS4**) compared to propagation. Therefore, the computation suggests that a highly structurally regular alkyne backbone might be efficiently obtained.

The predicted regioselectivity was experimentally supported by a proof-of-concept reaction, where **M1** underwent efficient tandem α-addition/ring-opening in a radical trifluoromethylation reaction with a regioselectivity of greater than 20:1 (Figure 2c).[17] Compared to the trifluoromethyl radical, a malonyl radical is bulkier and less reactive, which is expected to give even higher regioselectivity during **M1** polymerization. On a side note, such a regioselective radical reaction of VDCPs is previously unknown and could be potentially useful for small molecules synthesis.

Encouraged by these results, we set out to test the radical polymerization of **M1** (Table 1). AIBN-initiated free radical polymerization (1.6 M in toluene) afforded **P1** smoothly with > 90% monomer conversion (Table 1, entry 1, $M_n = 14.9$ kg/mol, $Đ = 1.67$). Indeed, **P1** was found to possess a well-defined alkyne backbone. Traditional RROP monomers such as CKAs suffer from incomplete ring-opening at concentrated conditions, while increasing backbiting has been observed with VCPs at dilute conditions.[15g,18] For comparison, we performed the reaction in both bulk and diluted solution (entries 2 and 3). Complete ring-opening and no backbiting were observed regardless of the concentration, which corroborates with the computational study (Figure S4). Such a behavior of VDCP might bring potential advantages as new low-shrinkage monomers for restorative materials.[19]
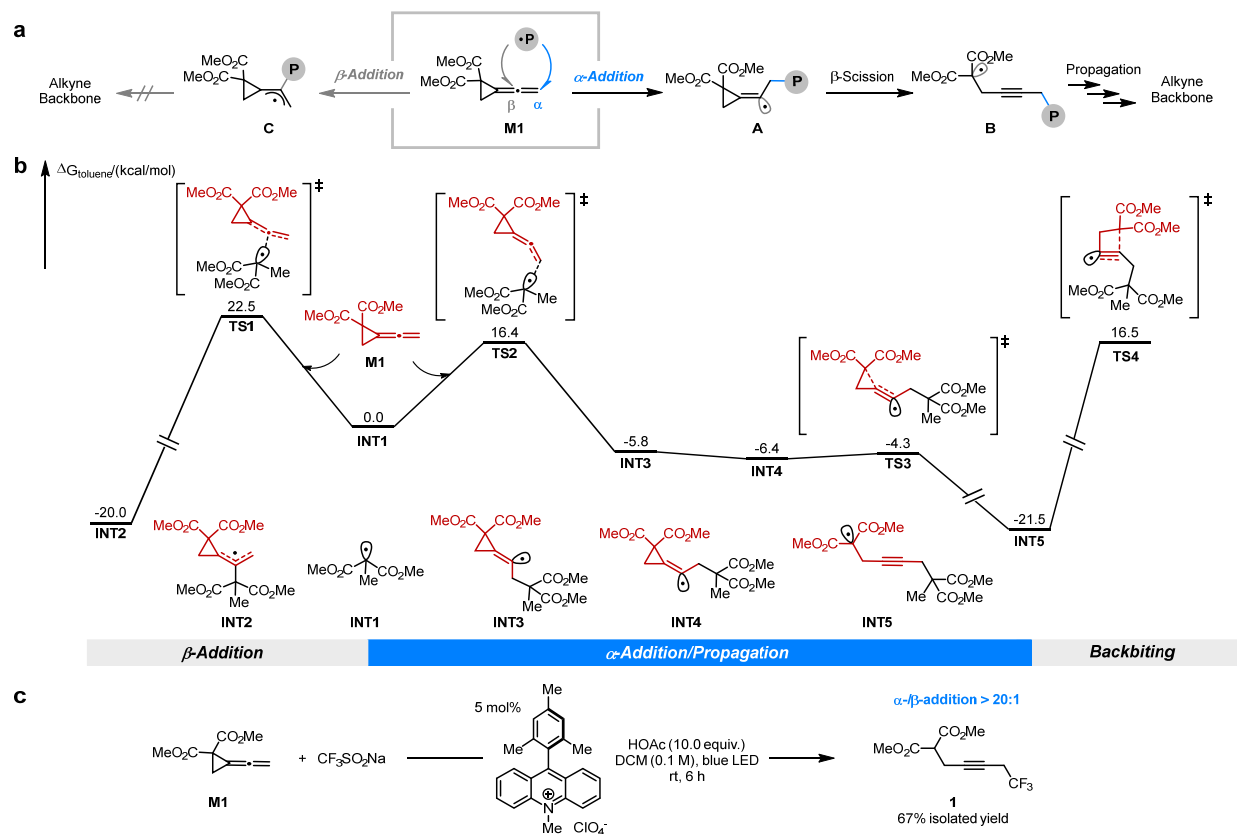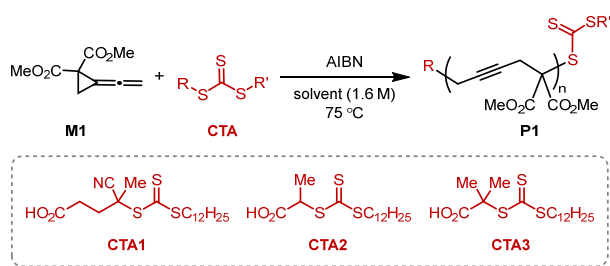

Figure 2. a) Possible pathways for the radical addition of **M1**. b) DFT calculations of the hypothesized reaction pathways. Computed at the SMD(toluene)/(U)M06-2X/def2-TZVPP//(U)B3LYP/6-31+G(d,p) level. c) Model reaction shows excellent regioselectivity for α-addition.

Table 1. Evaluation of polymerization conditions.[a]

Entry	[M1]:[CTA]:[AIBN]	CTA	Solvent	t/h	Conv.[b] (%)	M_n^c (kg/mol)	$Đ^c$
1	50:0:1	-	PhCH₃	12	93	14.9	1.67
2[d]	100:0:1	-	-	4.5	59	38.4	8.4
3[e]	50:0:1	-	PhCH₃	24	43	7.5	1.48
4	100:2:1	CTA1	PhCH₃	21	96	9.5	1.22
5	100:2:1	CTA2	PhCH₃	21	77	11.4	1.47
6	100:2:1	CTA3	PhCH₃	21	98	8.6	1.24
7	100:2:1	CAT1	PhCF₃	21	95	8.5	1.12
8	100:1:0.5	CAT1	PhCF₃	21	84	13.0	1.27
9	100:3:1	CAT1	PhCF₃	21	94	5.6	1.12
10	100:4:1	CAT1	PhCF₃	21	91	4.3	1.12

[a]Polymerization conditions: 0.40 mmol of **M1** was polymerized under nitrogen atmosphere at 75 °C and at concentration of 1.6 M, unless otherwise noted. The polymers were isolated by precipitation in MeOH. [b]Determined by ¹H NMR analysis of the combined liquid phases obtained from the precipitations. [c]Determined by GPC analysis calibrated against polystyrene standards. [d]Bulk polymerization at 0.80 mmol scale. [e][**M1**]₀ = 0.10 M.

We next focused on controlling the polymerization through reversible addition–fragmentation chain transfer (RAFT). Among three chain transfer agents (CTAs) evaluated (entries 4-6), **CTA1** was found superior in producing **P1** with good MW and narrow distribution. Solvents with different polarities were examined (Table S1) and PhCF₃ was identified as optimal (entry 7, M_n = 8.5 kg/mol, $Đ$ = 1.12). Consistent with a controlled polymerization, we lastly demonstrated that the MW of **P1** could be regulated by changing the **M1**/**CTA1** ratio (entries 8-10). In all cases, cyclic structures were not found in the polymer products.

The living characteristics of RAFT polymerization of **M1** were further evidenced by a first-order kinetics and a linear increase of M_n with respect to conversion (Figure 3a-c). The ¹H and ¹³C NMR spectra of a sample of **P1** ($M_{n,GPC}$ = 6.6 kg/mol, $Đ$ = 1.08) suggest the absence of allylic protons and alkenyl/cyclopropyl carbons, indicating exclusive α-addition, complete ring-opening and no backbiting cyclization (Figure 3d). The alkyne backbone was evidenced by the characteristic carbon signals at 77.7 ppm in ¹³C NMR spectrum as well as C≡C stretching bands in FTIR (2259 cm⁻¹, weak) and Raman (2242 cm⁻¹, strong) spectroscopy, respectively (Figure S13 and S14).
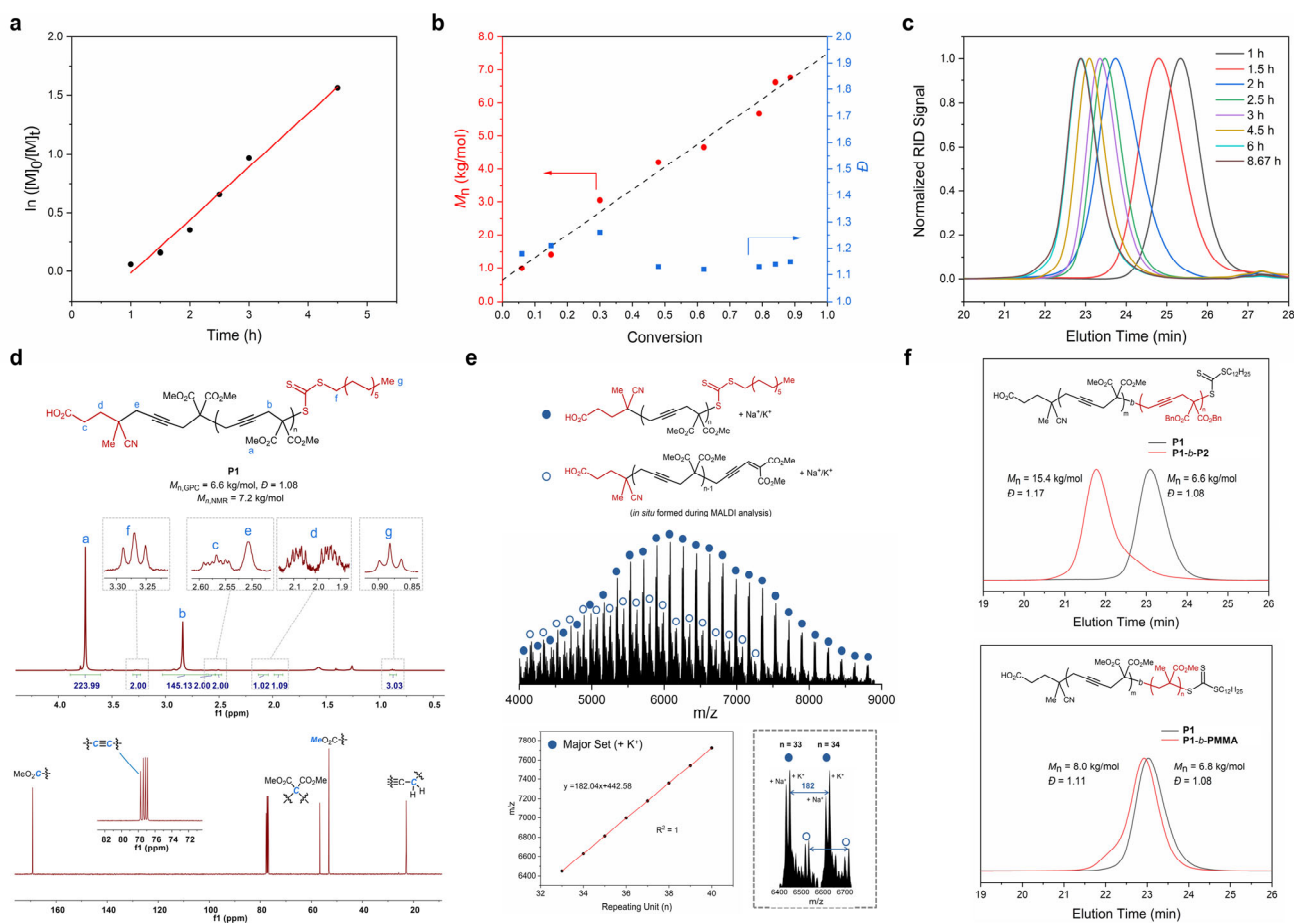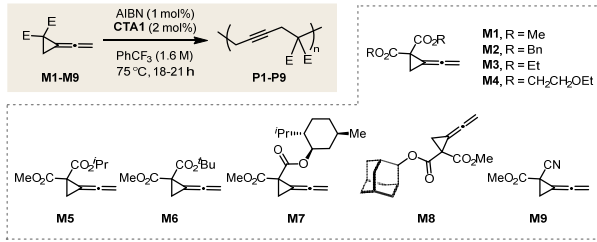

Figure 3. (a) Kinetic study of the RAFT polymerization of **M1**. (b) M_n and $Đ$ as functions of monomer conversion. (c) GPC traces of **P1** at different reaction times. (d) Assigned NMR spectra of **P1**. (e) MALDI-TOF analysis of **P1**. (f) Chain-extension polymerization from **P1** macroinitiators

A peak spacing that matches the assigned repeating unit was identified in matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectroscopy (Figure 3e). The major set of the peaks corresponded to a trithiocarbonyl group at the ω-end, whereas the minor set could be attributable to the *in situ* elimination of the same group during the MALDI analysis procedure.[20] This good chain-end fidelity corroborated with the ^{1}H NMR analysis, and the MW of **P1** estimated from NMR, GPC and mass spectroscopy were in good agreement. To further test the chain-end fidelity, chain extension experiments were performed using isolated **P1** as a macroinitiator (Figure 3f). Dibenzyl 2-vinylidenecyclopropane-1,1-dicarboxylate (**M2**) and methyl methacrylate (MMA) were employed for the synthesis of the second block, respectively. In both cases, the synthesis of block copolymers was supported by an increase of MW with narrow dispersity and ^{1}H NMR analysis (Figure S40 and S42).

With these results in hand, we next explored the monomer scope (Table 2). In general, VDCPs were easily prepared from corresponding malonates in one step and displayed decent thermal stability below 130 °C (Figure S1). The polymerizations of VDCPs bearing two identical ester groups were first examined (**M1**-**M4**). While the dimethyl and di(primary alkyl) dicarboxylates proved amenable to this protocol, a more hindered diisopropyl dicarboxylate led to a low conversion (Figure S39). Second, by fixing one tether as a methyl ester, we demonstrated that a series of bulky substituents on the other tether could be well tolerated (**M5**-**M8**). Pendant bulky groups such as those derived from menthol and admantane significantly increases the glass transition temperature (T_g) of the resulting polymer as determined by differential scanning calorimetry (DSC). Meanwhile, no melting peak was detected for any of the poly(VDCP)s, which contrasts with classical poly(VCP)s. Both the features are potentially desired for low-shrinkage materials. Third, a cyano-substituted monomer was polymerized in a good yield, albeit in an uncontrolled manner (**M9**). This might be attributable to the reduced stability of corresponding chain end. Poly(VDCP)s typically exhibit good thermal stability (T_d > 250 °C) except **P6** with a bulky *tert*-butyl groups and **P9** with a cyano group.

Table 2. Monomer Scope for RAFT polymerization of VDCPs.[a]

Entry	M	Conv. (%)[b]	Isolated Yield (%)	M_n (kg/mol)[c]	Đ[c]	T_g (°C)	T_d (°C)
1	**M1**	95	83	7.6	1.14	51	295
3	**M2**	90	86	9.1	1.28	23	304
2	**M3**	91	88	8.3	1.18	8	287
4	**M4**	97	80	13.8	1.22	-30	275
5	**M5**	96	82	12.0	1.17	38	279
6	**M6**	67	51	8.1	1.26	60	203
7	**M7**	89	83	12.1	1.16	85	286
8	**M8**	86	82	12.2	1.31	98	284
9[d]	**M9**	93	87	14.0	1.53	45	228

[a]Conditions: **M** (0.40 mmol), AIBN (1 mol %), **CTA1** (2 mol %), in 0.25 mL of PhCF₃ under nitrogen atmosphere at 75 °C for 18-21 h. [b]Determined by ^{1}H NMR analysis of the combined liquid phases obtained from precipitations. [c]Determined by GPC analysis calibrated against polystyrene standards. [d]1,4-Dioxane was used as the solvent.

In addition to thermally initiated RAFT polymerization, we envisioned that the photocontrolled polymerization of VDCP could be possible. Over the past decade, PET-ATRP has emerged as a powerful tool for the precise synthesis of polymers under mild conditions with spatial and temporal control.[21] To this, **M1** was found to be successfully polymerized in the presence of an Ir photocatalyst and an alkyl bromide initiator under blue light irradiation (Figure 4).[14c] Good temporal control was achieved as evidenced by the light on-off experiments.
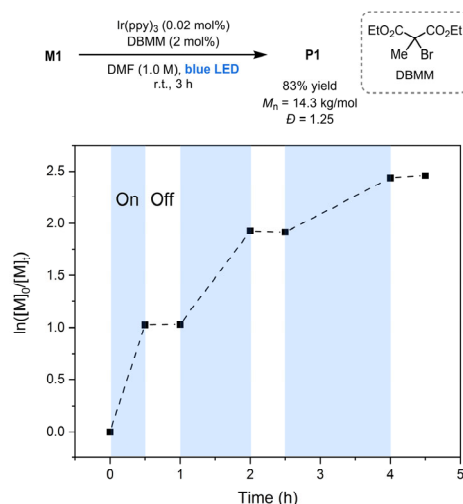

Figure 4. PET-ATRP of **M1** and ln([**M1**]$_0$/[**M1**]$_t$) as a function of reaction time with intermittent light exposure.

In conclusion, guided by their analogy with butatrienes, VDCPs have been identified as a new monomer class for radical ring-opening polymerization. They feature complete ring-opening and no back-biting regardless of polymerization conditions. A new metal-free strategy for the controlled synthesis of alkyne polymers with high structural regularity under RAFT polymerization and PET-ATRP conditions was established. This study shows that terminal-selective radical addition of allenic monomers can be achieved through stereoelectronic control, which is anticipated to facilitate future development of the radical chemistry of allenes, in the context of both polymer and small molecule synthesis.

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Notes

The authors declare no competing financial interest.

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