Polymerizations Initiated by Diradicals from Cycloaromatization Reactions

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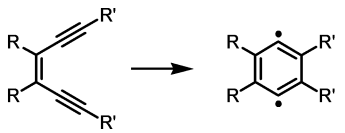
ABSTRACT: Four cycloaromatization substrates each produce diradicals that lead to the initiation of polymerization of vinyl monomers. All the initiators produce significant amounts of polymer, especially with methacrylate monomers. Intramolecular termination of short diradical chains produces oligomeric byproducts and limits the amount of high polymer that is formed. The polymer yield can be increased through the addition of a chain transfer agent by presumably converting unproductive diradicals into pairs of monoradicals. The enediynes that contain terminal acetylenes are less effective initiators because they retard radical polymerization. Bergman cyclization substrates are better initiators than Myers cyclization substrates.

Introduction

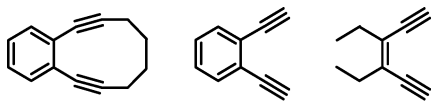
Soon after the first reports of radical polymerization, Flory promoted the idea of growing two polymer chains from a single diradical molecule.[1] At that time, the thermal initiation of styrene was presumed to occur through a diradical intermediate, and this hypothesis led to significant study and debate regarding diradical-initiated polymerizations.[1−6] Eventually, it was generally accepted that thermal initiation of styrene results primarily from monoradicals,[7] but the role of diradicals in styrene's autoinitiation is still under research.[8] Other diradical-initiated polymerizations have also been actively studied over the past half century. However, the diradicals previously studied including those from cyclic azo compounds,[9−11] tetraoxanes,[12] and electronically destabilized cyclopropanes[11,13,14] have all failed to produce significant amounts of polymer.

A more recently developed source of diradicals is the Bergman cyclization of enediynes to produce dihydroarenes (eq 1).



(1)

While this reaction has received significant attention in synthetic and biochemical applications,[15,16] its use in materials has been limited to homopolymerizations of enediynes to produce polyarenes or similar polymers.[17−23] Until our recent communication,[24] polymer initiation of vinyl monomers through Bergman cyclization appears only in the patent literature.[25] In contrast to the negative precedents in diradical-initiated polymerizations, our work with 3,4-benzocyclodec-3-ene-1,5-diyne (**1**)[26] demonstrated that diradicals formed from the Bergman cyclization of this enediyne could initiate significant radical polymerization.[24]



1 **2** **3**

However, the behavior of these polymerizations was unusual.[24] The polymer yields depended heavily on the type of monomer, with methacrylates producing significantly more polymer than styrene, methyl acrylate, or other monomers. In addition, the polymer had a bimodal molecular weight distribution. Mass spectrometry showed that the shorter-chain fraction was consistent with intramolecular termination of diradical intermediates while mechanistic studies showed that the high molecular weight fraction was formed from monoradical chain growth. The mechanism that is most consistent with these observations involves two competing reaction routes for the diradicals formed from the initiator.

In the first route, the diradicals can add to monomer units until the chain ends are sufficiently mobile to interact with each other and intramolecularly terminate. This route is the source of the low molecular weight fraction. The kinetics of this intramolecular termination have long been predicted to be extremely fast relative to polymer growth from both radicals.[5,6]

In the second route, one of the two radicals intermolecularly abstracts a hydrogen atom, and two monoradical molecules are formed. These monoradicals can then diffuse apart and produce high molecular weight polymer as in typical radical polymerizations.[27] This mechanism predicts that additives which favor hydrogen atom abstraction should produce more monoradical molecules and, therefore, more high polymer. This prediction was confirmed in polymerizations initiated by **1** in which the addition of butanethiol as a chain transfer agent produced dramatically higher yields of polymer than analogous polymerizations without the thiol.[24] Monomers that tend to favor chain transfer also produce good polymer yields.

Here we report a systematic comparison of polymerizations initiated by **1** and three other enediyne molecules with significant structural differences and two distinct cycloaromatization reactions. Through these studies, we demonstrate that the behavior we originally reported for **1** is general for several related diradical sources and for various monomers. In addition, we investigate some of the structural features of these initiators that favor polymerization.

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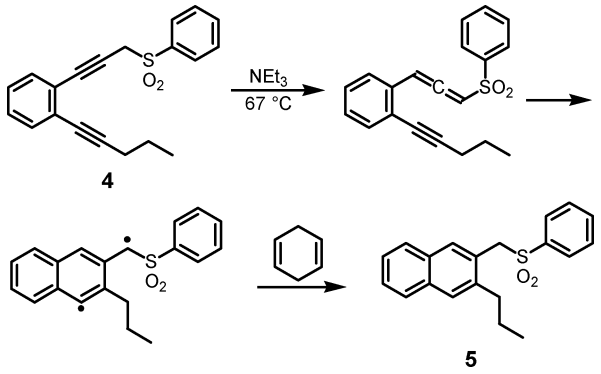
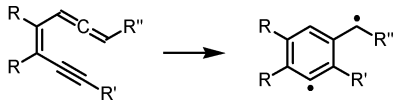
Scheme 1



The enediynes chosen for these experiments were constrained to cyclize at moderate temperatures (<160 °C) but also to be stable at room temperature. Enediynes with internal acetylene groups tend to cyclize only at very high temperatures, so they are not sufficiently reactive.[28] However, enediynes with terminal acetylene groups cyclize in the appropriate temperature range. 1,2-Diethynylbenzene (**2**), which cyclizes with a half-life of about 1 h at 152 °C,[28] was chosen to represent the class of benzannulated enediynes having terminal acetylenes. (*Z*)-2,3-Diethylhexa-l,5-diyn-3-ene (**3**) was chosen to represent the class of olefinic enediynes having terminal acetylenes.[29] While the kinetics of cyclization for this compound are not reported, a close structural analogue cyclizes with a half-life of about 2 h at 132 °C.[29]

To probe the effects of alternative diradical geometry, a substrate for Myers cyclization was chosen. Myers cyclization is the rearrangement of an eneyneallene to form an aromatic ring with one radical on the ring and another radical in a benzyl position (eq 2).



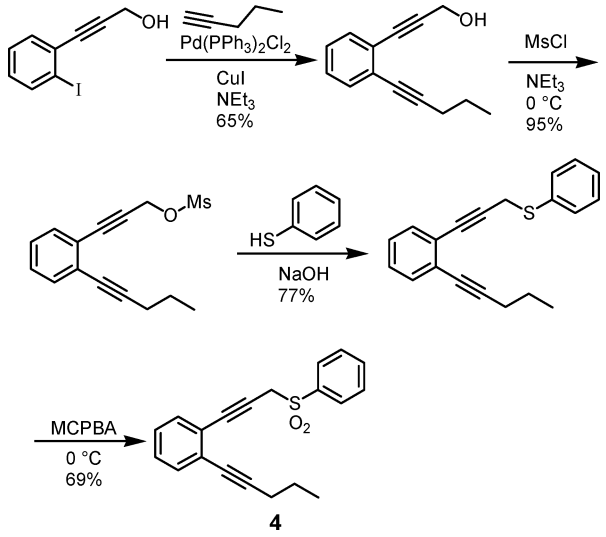
(2)

The lower activation energy of these cyclizations relative to Bergman cyclizations could lead to initiation of polymerization at much lower temperatures.[16] However, the higher reactivity of eneyneallenes also leads to instability that makes them less convenient to work with. To avoid this problem, a stable enediyne (**4**) with a propargylic sulfone group was used as an eneyneallene precursor. This class of compounds is known to rearrange to eneyneallenes under basic conditions.[30] Thus, we surmised that with the addition of mild base (e.g., amine) the eneyneallene would form, which would then rapidly undergo Myers cyclization to produce a diradical intermediate (Scheme 1).

Results and Discussion

Enediyne **4** was synthesized through the route established by Grissom and co-workers for similar compounds (Scheme 2).[30,31] DSC traces of **4** with and without added triethylamine confirmed that it is stable to more than 200 °C as the enediyne, but with the addition of the amine it reacts rapidly at temperatures above 60 °C. To confirm that this reaction was the desired cycloaromatization, enediyne **4** was mixed with 5 equiv of triethylamine and an excess of 1,4-cyclohexadiene (as a hydrogen atom donor). The primary product of this

Scheme 2



reaction was the expected naphthalene derivative **5** (Scheme 1).

At this point, all four of the enediynes in this study had been confirmed to undergo cyclizations that produce diradicals, but to meaningfully compare their behavior as initiators, their differences in reactivity had to be considered. Therefore, in situ ^{1}H NMR trials were used to measure the cyclization kinetics at various temperatures and to determine the temperatures at which each substrate cyclizes with a half-life of 16−20 h (Figure 1). The desired rates of Bergman cyclization for **1**, **2**, and **3** were achieved at 100, 120, and 104 °C, respectively. With the addition of 5 equiv of triethylamine, enediyne **4** was found to rearrange with the desired rate and undergo Myers cyclization at only 32 °C. By performing the comparative experiments at these specified temperatures, the rates of radical production will be approximately constant for all the tested enediynes. Thus, any differences in behavior observed between the initiators cannot be attributed to differences in cyclization rate.

The ability of the enediynes to initiate polymerizations was investigated by heating them in neat monomer at their specified temperatures (Table 1). Polymerizations of styrene and methyl acrylate were not performed with initiator **2** because the high temperature required (120 °C) produces excessive amounts of thermally initiated polymer in control reactions. The polymer yields achieved in this system varied greatly with the monomers that were employed, and specifically, the methacrylates gave the best conversions (vide infra).

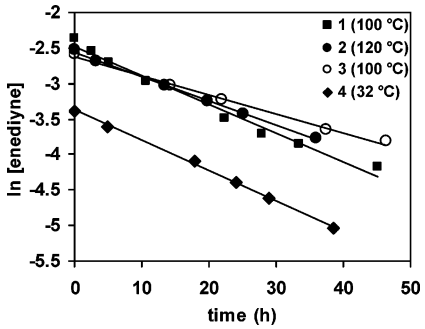


Figure 1. Kinetics of disappearance of the enediynes as measured by ^{1}H NMR in d_8-toluene with 1,4-cyclohexadiene (1 M). In the case of **4**, 5 equiv of triethylamine was added.

Table 1. Polymerizations Initiated by Enediynes[a]

monomer	initiator	[initiator] (mM)	T (°C)	polymer yield (%)	M_n	PDI
butyl methacrylate	**1**	22	100	93	714 000	1.38
	2	23	120	16	933 000	2.47
	3	25	104	3	338 000	1.59
	4	22	32	5	805 000	2.10
	none	0	100	2	1 129 000	1.21
methyl methacrylate	**1**	27	100	87	482 000	2.52
	2	29	120	5	760 000	2.82
	3	31	104	2	519 000	1.73
	4	23	32	4	499 000	2.29
	4	33	57	36	328 000	2.18
	4	36	82	45	284 000	2.78
	none	0	100	2	1 589 000	2.07
methyl acrylate	**1**	21	100	29	626 000	1.89
	3	24	104	1	228 000	1.58
	4	28	32	2	607 000	4.48
	none	0	100	18	3 441 000	2.22
styrene	**1**	24	100	12	265 000	1.84
	3	24	104	5	233 000	1.49
	4	22	32	1	101 000	7.61
	none	0	100	5	312 000	2.35
acrylonitrile	**1**	30	100	3		
	2	26	120	1		
	3	26	104	1		
	4	32	32	1		
	none	0	100	*b*		
vinylidene chloride	**1**	26	100	1		
	2	34	120	1		
	3	34	104	1		
	4	25	32	1		
	none	0	100	*b*		

[a] 2.5 h in neat monomer. [b] Trace.

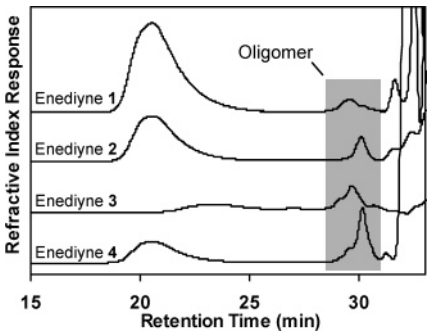


Figure 2. GPC traces from MMA polymerizations initiated by each enediyne.

Also, compared to the other enediynes, initiator **1** produces significantly more polymer with all tested monomers. These trials, particularly in the case of the methacrylates, demonstrate generally that the cycloaromatizations can be used to produce high polymer.

The previously observed intramolecular cyclization behavior was then investigated for each substrate.[24] As seen in Figure 2, each poly(methyl methacrylate) (PMMA) sample produced from the enediynes shows a bimodal distribution. The low molecular weight fractions are consistent with the theoretical kinetic analyses that suggest that intramolecular termination is the most likely result for polymer chains having radicals at both ends.[5,6] Because the chains are not predicted to grow extensively before intramolecular termination, observable amounts of oligomeric material are expected from this termination.

To confirm this interpretation, the oligomeric fractions in each case were isolated. Field desorption mass spectrometry revealed that these products are chains of initiator molecules and monomer units with no additional chain end groups (i.e., hydrogen atoms), and this molecular weight profile is consistent with intramolecular termination of diradical intermediates (Table 2).

To better understand this intramolecular termination process, individual compounds were isolated from similar oligomeric fractions and characterized. We previously reported structures **6** and **7** that were obtained from vinylidene chloride and **1**.[24] A similar experiment with acrylonitrile produced compound **8** (Figure 3) as well as at least eight other trimeric isomers that were not separable. All of these structures are consistent with diradical intermediates that intramolecularly terminate.

This intramolecular termination limits the production of high molecular weight polymer. However, if the diradical intermediates undergo chain transfer to another molecule before they intramolecularly terminate, then two monoradical molecules are formed which each have the potential to produce high polymer. Therefore, the addition of chain transfer agents to these reactions should facilitate monoradical formation and lead to higher yields of polymer. This hypothesis was tested by adding butanethiol to MMA polymerizations initiated by each enediyne. In all cases, the addition of butanethiol increases the polymer yields significantly (Figure 4). In a control case without enediynes, butanethiol increases the polymerization rate only slightly. While the small increases seen with the control are similar to those seen with **4**, the data for **4** were taken at a much lower temperature than the control, and a comparison between these two series should not be made.

To confirm that this enhancement is general for monomers other then MMA, enediyne **1** was used to initiate a similar series of polymerizations with different monomers. The results (Figure 5) show that higher concentrations of butanethiol lead to faster conversion of monomer in all cases. The chain transfer agent's dramatic effect on the rate of polymerization in this

Table 2. FDMS Data for MMA Oligomers Formed through Intramolecular Termination

	enediyne **1**		enediyne **2**		enediyne **3**		enediyne **4**	
monomer units	FW[a] (g/mol)	relative abundance (%)	FW[a] (g/mol)	relative abundance (%)	FW[a] (g/mol)	relative abundance (%)	FW[a] (g/mol)	relative abundance (%)
1	280	<2	226	<2	232	6	422	14
2	380	10	326	2	332	7	522	100
3	480	100	426	100	432	100	622	2
4	580	10	526	38	532	14	722	<2
1[b]	360	<2	252	<2	264	4	644	<2
2[b]	460	<2	352	<2	364	15	744	<2
3[b]	560	<2	452	3	464	11	844	<2

[a] Molecular weights of one initiator molecule and the shown number of monomer units. [b] These peaks correspond to two enediyne molecules. It is assumed that one of the endiynes acts as monomer, and it is counted as one of the listed number of monomer units.

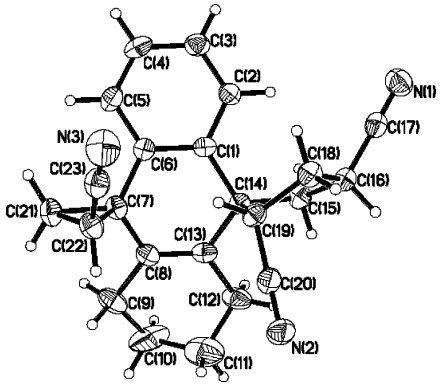


Figure 3. ORTEP drawing of oligomeric byproduct **8** resulting from the reaction of enediyne **1** with acrylonitrile.

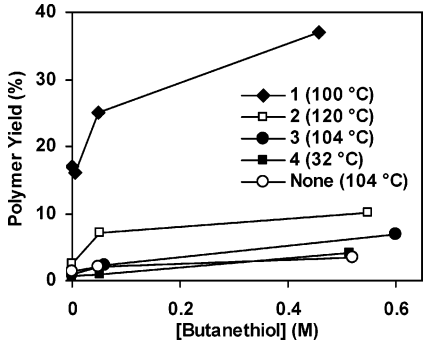


Figure 4. Effect of butanethiol on polymerizations with enediynes (6 mM) in neat MMA at 100 °C for 1 h. In the case of **4**, 5 equiv of triethylamine was added relative to the enediyne.

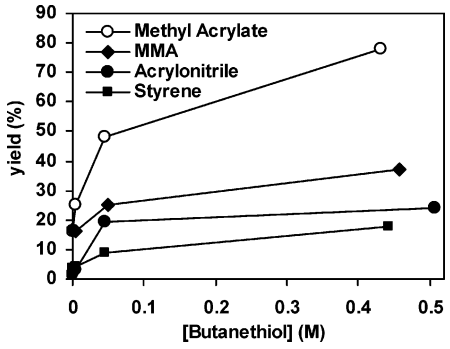


Figure 5. Effect of butanethiol on polymerizations with **1** (6 mM) in neat monomer at 100 °C for 1 h.

system supports the theory that the high polymer results from unproductive diradicals being converted to pairs of monoradicals via chain transfer.

The general mechanism of these diradical-initiated polymerizations may explain the dramatic monomer dependence in these reactions (Table 1). The key step required for polymer growth is the conversion of diradicals into pairs of monoradicals. Therefore, monomers that most favor chain transfer are expected to be those that produce the most polymer. Unfortunately, the transfer constants to monomer (C_M) cannot be used to make good predictions in this system because they do not account for the highly reactive radicals that are initially formed on the aromatic rings. If it is reasonably assumed that the didehydroarenes behave like phenyl radicals,[15] then hydrogen atom abstraction is more likely to occur with the aromatic radicals than with the monomer-derived radicals.[32] Unfortunately, the relative abilities of aromatic diradicals to abstract hydrogen atoms from different monomers is not known. However, because of the formation of a stabilized allylic radical, it seems reasonable that hydrogen atom abstraction from methacrylates would be more favorable than abstraction from monomers without an α-methyl group. This claim is supported by the report that *tert*-butoxy radicals can abstract hydrogen atoms from α-methyl groups of methacrylates with the ratio of abstraction to radical addition being as high as 0.63.[33] Although the radicals resulting from cycloaromatizations are significantly different from *tert*-butoxy radicals, similar abstraction of the relatively labile α-methyl hydrogen atoms is not unreasonable. The facility of this hydrogen atom abstraction from the α-methyl group is the most likely cause of the high polymer yields achieved with the methacrylates.[34]

While the enediynes in this study share the general behaviors that were just discussed, they also show significant differences. The most obvious of these differences is the efficiency with which they initiate polymerization. As seen in Table 1, enediyne **1** leads to much higher polymer yields than the other enediynes.

Apparently, **2** and **3** are poor initiators relative to **1** because of their tendency to retard polymerizations. Phenylacetylene retards MMA and styrene polymerizations as it copolymerizes with them.[35,36] Because of the structural similarity between phenylacetylene and enediynes having terminal acetylenes (i.e., **2** and **3**), it seemed likely that they would behave similarly. To measure possible retardation, MMA polymerizations in the presence of enediynes and AIBN were monitored at 60 °C using in situ ^{1}H NMR (Figure 6). At this temperature, none of the enediynes cyclize appreciably, so they are not expected to contribute to initiation. Therefore, the polymer is initiated only by the radicals produced from AIBN, and the effects of the enediynes are limited to side reactions. By comparing the rates in the presence of the enediynes with the control case with only AIBN, the retardative effects could be observed (Table 3).

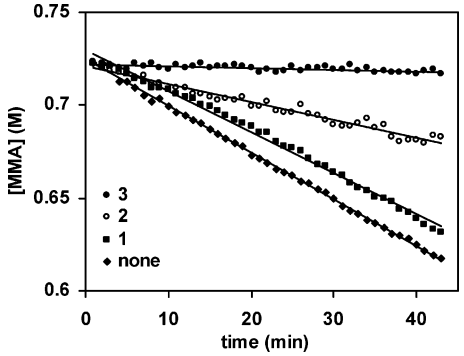


Figure 6. Copolymerization of MMA and enediynes initiated by AIBN (190 mM) at 60 °C monitored by in situ ^{1}H NMR.

Table 3. MMA Polymerization Rates in the Presence of Enediynes[a]

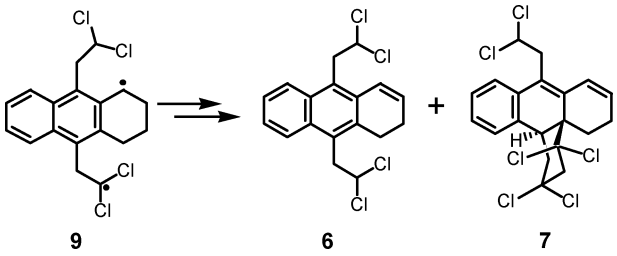
enediyne	relative R_p
none	1.00
1	0.88
2	0.38
3	0.03
4	1.00
1,2-dipent-1-ynylbenzene	1.08

[a] Performed at 60 °C in d_6-benzene. [Enediyne] = 75 mM, [MMA] = 720 mM, [AIBN] = 190 mM.

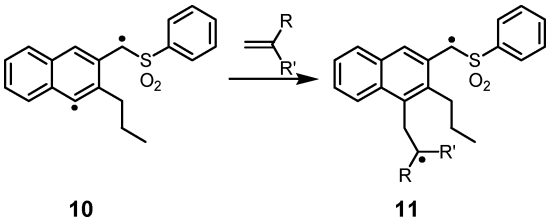
Clearly, the enediynes with terminal acetylenes (**2** and **3**) significantly retard the polymerizations, while **1**, **4**, and 1,2-dipent-1-ynylbenzene show no variation outside of experimental error. This suggests that the terminal alkynes are susceptible to attack by MMA-derived radicals while the internal alkynes are not. If this is the case, then **2** and **3** will be consumed during the polymerizations while the other enediynes will not be affected. By monitoring the concentrations of the enediyne during the experiments above, this hypothesis was confirmed. Only the enediynes with terminal acetylenes are consumed significantly. Additional evidence for the behavior of **3** as a comonomer is seen in the molecular weights of the MMA oligomers that were formed through intramolecular termination (Table 2). In the case of **3**, some of these oligomers have molecular weights consistent with a diradical that added to another initiator molecule as well as monomer before terminating. These kinetics measurements lead to the overall conclusion that **2** and **3** (and, in all likelihood, other enediynes bearing terminal acetylenes) are poor initiators of radical polymerization because of their tendencies to copolymerize and act as retarders.

The difference in polymer production between **1** and **4** is not explained by the copolymerization and retardation that complicate the use of **2** and **3**, so another significant effect must be involved. To confirm that this effect is not due to the large difference in the temperatures at which **1** and **4** were tested, enediyne **4** was used to initiate polymerizations at 57 and 82 °C (Table 1). Thus, a comparison between the two initiators can be made with less dependence on temperature. Of course, by increasing the temperatures above 32 °C, the cyclization of **4** is expected to be much faster than that of **1** at 100 °C, so the rates of radical formation are no longer equivalent. The higher rate of radical production with **4** is reflected in the lower molecular weights of its products. However, the yields achieved with **4** were still considerably lower than those with **1**. The lower molecular weight achieved with **4** despite its slower polymerization is consistent with a system where the

Scheme 3



Scheme 4



radical concentration is high, but many of the radicals do not initiate polymerization. Thus, the relatively rapidly forming diradicals from **4** may be undergoing significantly more intramolecular termination than those formed from **1**.

This hypothesis is supported by the mass spectrometry data on the isolated oligomeric MMA (Table 2). The Bergman cyclization substrates (**1**, **2**, and **3**) produce oligomers mostly composed of an initiator molecule with three added monomer units. In contrast, the Myers precursor **4** primarily produced initiator molecules with only one or two added monomer units. The difference in behavior may result from the different geometries of the respective diradicals. This argument is best illustrated through the oligomeric products **6** and **7** which were both likely formed through a common intermediate (**9**) having a benzylic radical (Scheme 3). Once this benzylic radical is formed, intramolecular termination appears to be very favorable. Because the eneyneallene derived from **4** forms a benzylic radical (**10**) as it cyclizes, it requires only one monomer addition step to reach the intermediate **11** (Scheme 4). Diradical **11** is closely analogous to diradical **9**, so it would similarly be expected to strongly favor intramolecular termination. This facilitated route to intramolecular termination limits the opportunities for **10** to undergo intermolecular hydrogen atom abstraction, so **4** results in fewer productive pairs of monoradicals and less polymer.

Conclusions

While the Bergman and Myers cyclization products can initiate radical polymerization, these reactions are complicated by the diradical nature of the initiators. In particular, the diradicals tend to terminate intramolecularly to produce oligomeric byproducts. By favoring hydrogen atom abstraction events that convert the diradicals into pairs of monoradicals, this intramolecular termination can be avoided and high polymer can be produced.

In comparing various enediynes, it was found that those with terminal acetylenes tend to retard radical polymerizations. Also, the diradicals produced through Myers cyclization have a geometry that seems to favor intramolecular termination more than those produced by Bergman cyclization. Therefore, Bergman cyclization

of enediynes having internal alkynes appears to be the most favorable cycloaromatization reaction for polymer initiation.

Experimental Section

Methyl methacrylate, butyl methacrylate, methyl acrylate, styrene, acrylonitrile, methacrylonitrile, and vinylidene chloride (all from Aldrich) were dried over CaH_2 and distilled prior to use. Triethylamine, methylene chloride, benzene, and chlorobenzene (all from Fisher) were similarly dried over CaH_2 and distilled. AIBN was recrystallized from MeOH. $Pd(PPh_3)_2Cl_2$ (Aldrich, 98%), CuI (Aldrich, 98%), 1-pentyne (Aldrich, 99%), methanesulfonyl chloride (Aldrich, 99.7%), thiophenol (Aldrich, 99%), *m*-chloroperoxybenzoic acid (Aldrich, ~70%), 1,4-cyclohexadiene (Aldrich, 97%), and anthracene (97%) were used as received. Anhydrous toluene (Aldrich, 99.8%) and anhydrous THF (Aldrich, 99.9%) were used as received. The other solvents were used as received from Fisher without purification or rigorous exclusion of moisture.

Gel permeation chromatography (GPC) measurements were performed in THF at 25 °C with a Waters 515 HPLC pump, a Viscotek TDA model 300 triple detector, and a series of three Viscogel 7.8 × 300 mm columns (2 × GMHXL16141 and 1 × G3000HXL16136). Molecular weight data were determined using Viscotek's TriSEC software. The light scattering, mass, and viscosity constants were determined from a single 96 kDa narrow polystyrene standard and checked against other known polystyrene standards for accuracy. The column exclusion limit was 1.0×10^7 Da, and the flow rate was 1.0 mL/min. ^{1}H NMR spectra were taken on a Varian Unity 500 instrument. Mass spectrometry was performed on a Micromass 70-VSE instrument in FD mode.

General Polymerization Procedure. The enediyne (0.022 mmol) was weighed into an oven-dried Schlenk tube and placed under a nitrogen atmosphere. Monomer (1 mL) was then injected into the tube, and the solution was degassed through three consecutive freeze−pump−thaw cycles. To account for any monomer lost during the degassing cycles, the tube was weighed and the amount of monomer remaining was calculated by comparison with the weight of the empty tube. The solution was placed in an oil bath at the appropriate temperature for 2.5 h. In some cases, monomer was heated above its boiling point in these sealed systems, and extreme caution must be used due to the pressure that develops. The resultant poly(methyl methacrylate), poly(butyl methacrylate), and polystyrene samples were dissolved in THF and precipitated into MeOH. Poly(methyl acrylate) samples were dissolved in THF and precipitated into petroleum ether. Polyacrylonitrile and poly(vinylidene chloride) were isolated by removing residual monomer under vacuum.

Representative Polymerization of MMA Initiated by 1. Enediyne **1** (3.9 mg, 0.022 mmol) was weighed into an oven-dried Schlenk tube and placed under a nitrogen atmosphere. Methyl methacrylate (1.0 mL) was then injected into the tube, and the solution was degassed through three consecutive freeze−pump−thaw cycles. To account for any MMA lost during the degassing cycles, the tube was weighed and the amount of monomer remaining (0.764 g, 7.6 mmol) was calculated by comparison with the weight of the empty tube. The solution was placed in an oil bath at 100 °C for 2.5 h. The resultant PMMA was dissolved in THF and precipitated into MeOH. The precipitate was collected by filtration and dried under vacuum to give a white polymer (0.668 g, 87%). GPC (g/mol): M_n = 482 000, M_w = 1 215 000.

General Oligomerization Procedure. The appropriate enediyne (0.22 mmol) was weighed into an oven-dried Schlenk tube and placed under a nitrogen atmosphere. Chlorobenzene (18 mL) and methyl methacrylate (1.88 g, 18.8 mmol) were added via syringe. The solution was degassed with three consecutive freeze−pump−thaw cycles and placed in a 100 °C bath for 5 h. Nearly all the solvent and residual monomer were removed under vacuum. The product mixture was then dissolved in THF and precipitated into MeOH to remove the polymer. The filtrate was concentrated under vacuum. Residual initiator was removed through silica gel chromatography. The resulting oligomeric mixtures were analyzed by FDMS.

Representative Oligomerization of MMA Initiated by 1. Enediyne **1** (0.040 g, 0.22 mmol) was weighed into an oven-dried Schlenk tube and placed under a nitrogen atmosphere. Chlorobenzene (18 mL) and methyl methacrylate (1.88 g, 18.8 mmol) were added via syringe. The solution was degassed with three consecutive freeze−pump−thaw cycles and placed in a 100 °C bath for 5 h. Nearly all the solvent and residual monomer were then removed under vacuum. The resulting polymer/oligomer mixture was analyzed by GPC. The product mixture was then precipitated into MeOH from a THF solution, and the PMMA was removed by filtration and dried to give a white polymer (0.49 g, 26%). GPC (g/mol): M_n = 46 000; M_n = 78 000. The filtrate was concentrated under vacuum to yield crude oligomer (0.050 g). Residual initiator (0.011 mg, 0.06 mmol, 28%) was removed by column chromatography using a 1:4 mixture of methylene chloride and petroleum ether, respectively. The remaining oligomer was forced to elute from the column by using a 1:7:32 mixture of methanol, methylene chloride, and petroleum ether, respectively. A mixture of products was obtained. FDMS (*m/z*): 380 (10%), 480 (100%), 580 (10%).

Oligoacrylonitrile Formation (8). Enediyne **1** (98 mg, 0.55 mmol) was weighed into an oven-dried 100 mL Schlenk tube and placed under an Ar atmosphere. Acrylonitrile (10 mL, 0.152 mol) was added via syringe. The solution was degassed with three consecutive freeze−pump−thaw cycles and placed in a 100 °C bath for 20 h. DMF was added to disperse the polymer, which was then precipitated into MeOH and filtered to give 1.49 g of polymer (19%). The filtrate was evaporated to leave 189 mg of material that was separated by column chromatography (1:4:5 EtOAc/petroleum ether/ methylene chloride). 69 mg of trimeric products (FDMS *m/z* = 339) was isolated, but only one product (**8**) was isolated with sufficient purity for characterization. 12 mg, 7% (relative to **1**). ^{1}H NMR (500 MHz, CD_2Cl_2, δ): 7.54 (1 H, dd, J = 8, 1.1 Hz), 7.45 (1 H, ddd, J = 7.5, 7.5, 1.4 Hz), 7.40 (1 H, ddd, J = 7.5, 7.5, 1.3 Hz), 7.22 (1 H, dd, J = 7.7, 1.3 Hz), 3.49 (1 H, dddd, J = 11.6, 11.6, 7.1, 7.1 Hz), 3.19 (1 H, dd, J = 15.4, 11.6 Hz), 3.11 (1 H, d, J = 6.7 Hz), 2.75 (1 H, dd, J = 15.4, 6,6 Hz), 2.48 (1 H, dd, J = 13.4, 7.6 Hz), 2.46 (1 H, m), 2.26 (1 H, dd, J = 6.7, 6.7 Hz), 2.24 (1 H, m), 2.18 (1 H, ddd, J = 13.5, 11.5, 6.9 Hz), 2.09 (1 H, dd, J = 9.5, 7.2 Hz), 1.93 (1 H, m), 1.85 (1 H, dd, J = 9.5, 6.2 Hz), 1.81 (1 H, m), 1.71 (2 H, m), 1.69 (1 H, m), 1.60 (1 H, m). ^{13}C NMR (125 MHz, CD_2Cl_2, δ): 143.98, 138.22, 133.92, 132.49, 127.85, 127.55, 127.39, 125.45, 124.32, 123.65, 121.17, 119.27, 119.00, 41.81, 33.94, 33.80, 33.71, 29.01, 26.65, 26.29, 22.73, 22.04, 14.89.

Preparation of 3-(2-Pent-1-ynylphenyl)prop-2-yn-1-ol. In a 50 mL Schlenk tube, $Pd(PPh_3)_2Cl_2$ (98 mg, 0.14 mmol) and CuI (89 mg, 0.47 mmol) were dissolved in toluene (40 mL). 3-(2-Iodophenyl)-2-propyn-1-ol[31] (1.20 g, 4.65 mmol) and 1-pentyne (5.00 g, 73.4 mmol) were then added via syringe. The solution was degassed under vacuum, and triethylamine (2 mL, 14 mmol) was added. After stirring for 18 h, ethyl ether was added and the mixture was filtered. The solvent was removed and column chromatography with a 1:9 mixture of ethyl acetate and petroleum ether resulted in 600 mg (65%) of 3-(2-pent-1-ynylphenyl)prop-2-yn-1-ol as a dark orange oil. TLC R_f 0.45 (1:3 ethyl acetate/petroleum ether). FTIR (neat): 3347 (br), 3061, 2963, 2933, 2871, 2231, 1481, 1443, 1025, 758 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$, δ): 7.40 (m, 2H, ar), 7.22 (m, 2H, ar), 4.53 (s, 2H, −C**H$_2$**−OH), 2.45 (t, J = 6.9 Hz, 2H, −C**H$_2$**−CH_2−), 1.76 (br s, 1H, −O**H**), 1.65 (m, 2H, −C**H$_2$**−CH_3), 1.08 (t, J = 7.3 Hz, 3H, −C**H$_3$**). ^{13}C NMR (500 MHz, $CDCl_3$, δ): 132.2 (ar), 132.1 (ar), 128.4 (ar), 127.4 (ar), 126.8 (q, ar), 125.0 (q, ar), 94.9 (≡**C**−CH_2−), 90.8 (≡**C**−CH_2−), 84.9 (≡**C**−C−), 79.6 (≡**C**−C−), 52.0 (−CH_2−OH), 22.3 (−**C**H_2−), 21.8 (−**C**H_2−), 13.7 (−**C**H_3). HRMS-EI (*m/z*): M^+ calcd for $C_{14}H_{14}O$, 198.1045; found, 198.1047.

Preparation of Methanesulfonic Acid 3-(2-Pent-1-ynylphenyl)prop-2-ynyl Ester. Methanesulfonyl chloride (410 mg, 3.6 mmol) was added dropwise to a solution of 3-(2-

pent-1-ynylphenyl)prop-2-yn-1-ol (550 mg, 2.77 mmol) and triethylamine (390 mg, 3.9 mmol) in methylene chloride (14 mL) at 0 °C. After stirring for 1 h at 0 °C, filtration through a silica plug with a 1:1 mixture of ethyl acetate and petroleum ether gave 730 mg (95%) of the desired mesylate as a dark orange oil. FTIR (neat): 2964, 2936, 2873, 2231, 1482, 1444, 1365, 1177, 993, 974, 936, 803, 761 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$, δ): 7.42 (m, 2H, ar), 7.29 (m, 1H, ar), 7.23 (m, 1H, ar), 5.12 (s, 2H, $-C\mathbf{H_2}-O-$), 3.19 (s, 3H, $-S-C\mathbf{H_3}$), 2.44 (t, J = 7.0 Hz, 2H, $-C\mathbf{H_2}-CH_2-$), 1.65 (m, 2H, $-C\mathbf{H_2}-CH_3$), 1.08 (t, J = 7.3 Hz, 3H, $-C\mathbf{H_3}$). ^{13}C NMR (500 MHz, $CDCl_3$, δ): 132.5 (ar), 132.3 (ar), 129.4 (ar), 127.6 (ar), 127.4 (q, ar), 123.6 (q, ar), 95.6 ($\equiv\mathbf{C}-CH_2-$), 88.7 ($\equiv\mathbf{C}-CH_2-$), 84.1 ($\equiv\mathbf{C}-C-$), 79.3 ($\equiv\mathbf{C}-C-$), 58.8 ($-\mathbf{C}H_2-O-$), 39.5 ($-S-\mathbf{C}H_3$), 22.3 ($-\mathbf{C}H_2-$), 21.7 ($-\mathbf{C}H_2-$), 13.7 ($-\mathbf{C}H_3$). HRMS-EI (m/z): M^+ calcd for $C_{14}H_{14}O$, 276.0820; found, 276.0827.

Preparation of 1-Pent-1-ynyl-2-(3-phenylsulfanylprop-1-ynyl)benzene. A solution of NaOH in water (0.22 mL, 15 M, 3.3 mmol) was added to thiophenol (360 mg, 3.3 mmol) in THF (50 mL). A solution of methanesulfonic acid 3-(2-pent-1-ynylphenyl)prop-2-ynyl ester (650 mg, 2.35 mmol) in THF (5 mL) was then added dropwise to the thiophenol solution at room temperature, and the reaction was stirred for 1 h. Column chromatography with petroleum ether gave 522 mg (77%) of 1-pent-1-ynyl-2-(3-phenylsulfanylprop-1-ynyl)benzene as a yellow oil. TLC R_f 0.40 (1:19 ethyl acetate/petroleum ether). FTIR (neat): 3059, 2962, 2932, 2871, 2229, 1584, 1481, 1440, 1227, 758, 739, 690 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$, δ): 7.52−7.54 (m, 2H, ar), 7.38 (m, 1H, ar), 7.31−7.34 (m, 3H, ar), 7.17−7.26 (m, 3H, ar), 3.89 (s, 2H, $-C\mathbf{H_2}-S-$), 2.39 (t, J = 7.0 Hz, 2H, $-C\mathbf{H_2}-CH_2-$), 1.62 (m, 2H, $-C\mathbf{H_2}-CH_3$), 1.05 (t, J = 7.4 Hz, 3H, $-C\mathbf{H_3}$). ^{13}C NMR (500 MHz, $CDCl_3$, δ): 135.8 (q, ar), 132.2 (ar), 132.0 (ar), 130.4 (2C, ar), 129.1 (2C, ar), 128.1 (ar), 127.3 (ar), 127.0 (ar), 126.9 (q, ar), 125.5 (q, ar), 94.8 ($\equiv\mathbf{C}-CH_2-$), 88.9 ($\equiv\mathbf{C}-CH_2-$), 82.8 ($\equiv\mathbf{C}-C-$), 79.6 ($\equiv\mathbf{C}-C-$), 24.1 ($-\mathbf{C}H_2-S-$), 22.4 ($-\mathbf{C}H_2-$), 21.8 ($-\mathbf{C}H_2-$), 13.7 ($-\mathbf{C}H_3$). HRMS-EI (m/z): M^+ calcd for $C_{14}H_{14}O$, 290.1129; found, 290.1129.

Preparation of 1-(3-Benzenesulfonyl-prop-1-ynyl)-2-pent-1-ynylbenzene (4). A solution of 1-pent-1-ynyl-2-(3-phenylsulfanylprop-1-ynyl)benzene (652 mg, 3.78 mmol) in methylene chloride (3 mL) was added dropwise at 0 °C to a solution of *m*-chloroperoxybenzoic acid in methylene chloride (40 mL), and stirring was continued for 1 h at 0 °C. Column chromatography with a 1:4 mixture of ethyl acetate and petroleum ether followed by a second column with methylene chloride gave 247 mg (45%) of 1-(3-benzenesulfonylprop-1-ynyl)-2-pent-1-ynylbenzene as well as 209 mg of the corresponding sulfoxide. The sulfoxide was further oxidized under analogous conditions and purified with column chromatography using methylene chloride to give an additional 136 mg of the sulfone for a total yield of 69%. TLC R_f 0.60 (methylene chloride). FTIR (neat): 3062, 2963, 2934, 2905, 2872, 2230, 1481, 1447, 1326, 1167, 1139, 1086, 873, 761, 744, 688 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$, δ): 8.07 (m, 2H, ar), 7.68 (m, 1H, ar), 7.58 (m, 2H, ar), 7.38 (m, 1H, ar), 7.29 (m, 1H, ar), 7.25 (m, 1H, ar), 7.19 (m, 1H, ar), 4.22 (s, 2H, $-C\mathbf{H_2}-S-$), 2.38 (t, J = 7.0 Hz, 2H, $-C\mathbf{H_2}-CH_2-$), 1.58 (m, 2H, $-C\mathbf{H_2}-CH_3$), 1.01 (t, J = 7.3 Hz, 3H, $-C\mathbf{H_3}$). ^{13}C NMR (500 MHz, $CDCl_3$, δ): 138.1 (q, ar), 134.4 (ar), 132.4 (ar), 132.2 (ar), 129.3 (4C, ar), 128.9 (ar), 127.4 (ar), 127.2 (q, ar), 124.1 (q, ar), 95.3 ($\equiv\mathbf{C}-CH_2-$), 86.8 ($\equiv\mathbf{C}-CH_2-$), 80.1 ($\equiv\mathbf{C}-C-$), 79.2 ($\equiv\mathbf{C}-C-$), 49.9 ($-\mathbf{C}H_2-S-$), 22.2 ($-\mathbf{C}H_2-$), 21.7 ($-\mathbf{C}H_2-$), 13.7 ($-\mathbf{C}H_3$). HRMS-EI (m/z): M^+ calcd for $C_{14}H_{14}O$, 322.1028; found, 322.1026.

Myers Cyclization of 4 to 2-Benzenesulfonylmethyl-3-propylnaphthalene (5). A solution of **4** (20 mg, 0.062 mmol), 1,4-cyclohexadiene (0.50 mL, 423 mg, 5.3 mmol), and triethylamine (31 mg, 0.31 mmol) in benzene (2 mL) was stirred for 15 h at 37 °C followed by 23 h at 67 °C. Column chromatography with a 1:9 mixture of ethyl acetate and petroleum ether gave 12 mg (60%) of **5**. TLC R_f 0.21 (1:9 ethyl acetate/petroleum ether). ^1H NMR (500 MHz, $CDCl_3$, δ): 7.74 (d, J = 8.1, 1H, ar), 7.59−7.65, (m, 5H, ar), 7.40−7.49 (m, 5H, ar), 4.55 (s, 2H, $-C\mathbf{H_2}-S-$), 2.55 (t, J = 7.8 Hz, 2H, $-C\mathbf{H_2}-CH_2-$), 1.58 (m, 2H, $-C\mathbf{H_2}-CH_3$), 0.94 (t, J = 7.4 Hz, 3H, $-C\mathbf{H_3}$). ^{13}C NMR (500 MHz, $CDCl_3$, δ): 139.6 (q, ar), 138.3 (q, ar), 134.0 (ar), 133.7 (q, ar), 132.1 (ar), 131.7 (q, ar), 129.2 (2C, ar), 129.0 (2C, ar), 127.9 (ar), 127.8 (ar), 127.3 (ar), 126.9 (ar), 125.9 (ar), 125.0 (q, ar), 59.9 ($-\mathbf{C}H_2-S-$), 34.8 ($-\mathbf{C}H_2-$), 23.8 ($-\mathbf{C}H_2-$), 14.2 ($-\mathbf{C}H_3$). HRMS-EI (m/z): M^+ calcd for $C_{14}H_{14}O$, 324.1184; found, 324.1180.

Cyclization Kinetics Measurements. In a nitrogen-filled glovebox, the appropriate enediyne (0.079 mmol) and anthracene (5 mg, 0.028 mmol) were dissolved in d_8-toluene (0.71 mL). The tube was capped with a septum and removed from the glovebox. 1,4-Cylohexadiene (0.075 mL, 0.79 mmol) was added via syringe. After an initial spectrum was taken, the tube was placed in a heated oil bath. The tube was briefly removed from the bath periodically to take NMR spectra. After approximately two half-lives, the rate of cyclization was calculated with first-order kinetics based on the amount of time that the sample had been in the oil bath. The concentration of enediyne was calculated based on the integrated signal of the anthracene internal standard.

AIBN-Initiated Polymerizations of MMA. A stock solution was prepared with AIBN (0.20 M) and anthracene (0.093 M) in d_6-benzene. NMR samples were prepared with this stock solution (0.60 mL), MMA (0.050 mL, 0.047 mmol), and the appropriate enediyne (0.049 mmol). A control sample with no enediyne was prepared with the same stock solution. The samples were capped with septa and removed from the glovebox. The solutions were heated to 60 °C in the NMR probe, and a spectrum was taken every minute. The concentrations of MMA and enediyne were calculated based on the integrated signals of the anthracene internal standard.

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Supporting Information Available: DSC data on the cyclization of **4**, UV absorbance data for PMMA initiated by **1**, kinetics of enediyne consumption in the presence of AIBN, and crystallographic data for **8**. This material is available free of charge via the Internet at http://pubs.acs.org.

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