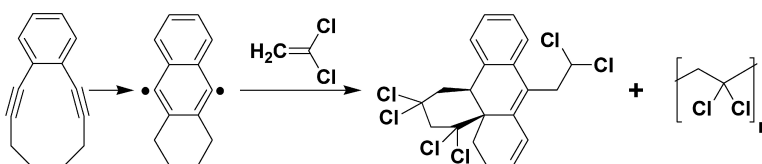


Radical Polymerization Initiated by Bergman Cyclization

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Radical Polymerization Initiated by Bergman Cyclization

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The possibility of initiating addition polymerization reactions with diradical sources has been debated since the early studies on thermally initiated polymerization of styrene. Simple theory predicts that short diradical polymer chains are more likely to undergo intramolecular termination than grow to high polymer.^{1,2} Significant efforts toward experimental confirmation of this theory have been made; potential diradical initiators in previous experiments have achieved only low levels of polymerization with some evidence for intramolecular termination.^{3–6}

The Bergman cyclization of enediyne is known to generate diradical intermediates that can undergo subsequent radical reactions.⁷ While homopolymerizations of Bergman cyclization products have been examined,⁸ the use of these dihydroarene diradicals to initiate polymerization of vinyl monomers is reported only in patent literature.⁹

Here, we report the use of a diradical generated in a Bergman cyclization to initiate radical polymerization (Scheme 1). Characterization of the oligomeric and polymeric products reveals how the diradical nature of the initiator affects polymerization; the observed behavior is in good agreement with theory that has existed for more than half a century.^{1,2}

The ability of diradical **2** to initiate polymerization was investigated by heating 3,4-benzocyclodec-3-ene-1,5-diyne¹⁰ (**1**) in neat monomer at 100 °C (Table 1). Control experiments in which monomer was heated without **1** resulted in polymer yields of less than 2% in all cases except methyl acrylate (18%) and styrene (5%). Polymerizations with **1** gave significantly larger polymer yields for all of the monomers studied.

Theoretical kinetic analysis of polymerizations involving diradical chains suggests that intramolecular termination and, under certain conditions, chain transfer are most likely. High polymer growth from both radicals is not predicted to be competitive with intramolecular termination and chain transfer. Thus, the only high polymer produced in a diradical-initiated system is expected to result from monoradicals formed after the diradical undergoes chain transfer with monomer, polymer, or other available chain transfer agents.²

To address whether the polymer growth in this system is occurring by propagation from two radicals per chain or only one, the relation between the degree of polymerization (DP) and the rate of polymerization (R_p) was examined according to an established method.³ For monoradical polymerization, it can be shown that

$$\frac{1}{DP} = C_M + C_1 \frac{[In]}{[M]} + AR_p \quad (1)$$

where $A = (2k_{td} + k_{tc})/(k_p[M])^2$, C_M and C_1 are the chain transfer constants to monomer and initiator, respectively, $[In]$ is the initiator concentration, $[M]$ is the monomer concentration, and k_p , k_{td} , and k_{tc} are the rate constants of propagation, termination by disproportionation, and termination by coupling, respectively. If chain transfer

Scheme 1

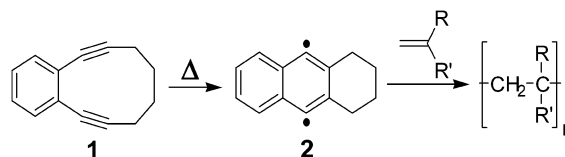


Table 1. Polymerization Initiated by Eneidyne **1**^a

monomer	[1] (mM)	yield (%) ^b	M_n^c	PDI
butyl methacrylate	22	93	714 000	1.38
methyl methacrylate	27	87	482 000	2.52
methyl acrylate	21	29	626 000	1.89
styrene	24	12	265 000	1.84
methacrylonitrile	31	7		
acrylonitrile	30	3		
vinylidene chloride	26	1		

^a Reactions ran for 2.5 h at 100 °C. ^b Yield of isolated polymer. ^c GPC data based on refractive index, viscometry, and light scattering.

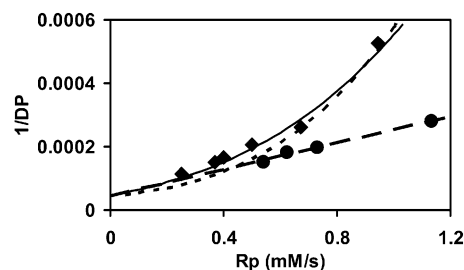


Figure 1. Chain length and rate data for MMA polymerizations at 100 °C: (●) initiation with azobis(cyclohexanecarbonitrile); (◆) initiation with enediyne **1**; (---) monoradical fit in absence of chain transfer to initiator; (- - -) monoradical fit accounting for chain transfer to initiator; (- - - -) diradical fit accounting for chain transfer to initiator.

to initiator is negligible, the second term in eq 1 can be ignored. In this case, a plot of $1/DP$ versus R_p will be linear and constant for all monoradical initiators when using the same monomer and identical reaction conditions.³

A plot of $1/DP$ versus R_p for the polymerization of methyl methacrylate (MMA) was generated using variable loadings of the monoradical initiator 1,1'-azobis(cyclohexanecarbonitrile). As expected, the plot was linear (Figure 1). The intercept of this line represents the transfer constant to monomer (C_M), and our value (4.2×10^{-5}) agrees very well with the reported value at 100 °C (3.8×10^{-5}).¹¹

In a diradical polymerization of MMA (if it is assumed that there is no intramolecular termination or transfer to initiator and that intermolecular termination occurs by disproportionation), the slope of the plot of $1/DP$ versus R_p is expected to be reduced by a factor of 2.³ Thus, this slope can be used to determine whether the polymerizations initiated by enediyne **1** are growing from one radical per chain or two. When the plot for polymerizations initiated by **1** was constructed, a deviation from linearity was observed

(Figure 1). This indicates that C_1 is not negligible and the radical intermediates undergo chain transfer to the initiator or primary radical termination.

Assuming either diradical propagation or monoradical propagation, two provisional values for C_1 were calculated for polymerizations initiated by enediyne **1**.³ These C_1 values were then used with eq 1 to fit the experimental data. It can be seen that the monoradical curve is in better agreement with the experimental values (Figure 1), so propagation appears to proceed primarily from a single radical.

Significant intramolecular termination of the diradical chains should produce observable amounts of oligomeric material, and such products were observed in polymerizations initiated by **1**. In the case of MMA, these oligomers were observed by gel permeation chromatography (GPC). The chromatogram showed a bimodal distribution with a large peak corresponding to high polymer ($M_n = 46\,000$) and a smaller peak corresponding to oligomer ($M_n \approx 500$). The oligomer peak ($M_n \approx 500$) was absent in control experiments involving homopolymerization of **1** and with monoradical initiation of MMA using 1,1'-azobis(cyclohexanecarbonitrile).

Oligomers of both MMA and vinylidene chloride (VC) that were produced with diradical initiation were isolated by a combination of fractional precipitation and column chromatography. The oligomeric MMA was only isolable as a mixture, and field desorption mass spectrometry of this mixture gave three signals at $m/z = 380.2$ (10%), 480.3 (100%), and 580.4 (10%). These values are in good agreement with the calculated m/z values of 380.20, 480.25, and 580.30 corresponding to a molecule of initiator (**1**) and two, three, and four MMA units, respectively. The oligomer mixture shows a UV absorbance peak at 291 nm which is consistent with the naphthalene product expected from Bergman cyclization. The ¹H NMR spectrum of this mixture was complex due to the number of compounds and stereoisomers present, but it was qualitatively consistent with oligomeric MMA.

When VC was used as the monomer, the two main components (Figure 2) of the oligomeric fraction were found to be dimer **3** (14% relative to **1**) and trimer **4** (5% relative to **1**, structure confirmed crystallographically). Clearly, these products are both consistent with diradical intermediates in which the initial aryl radicals each add across VC.

If chain transfer products are the primary source of high polymer in this diradical-initiated polymerization, then the addition of chain transfer agent should increase the rate of polymerization. This was confirmed with the polymerization of acrylonitrile (AN). A polymerization of AN initiated by **1** gave only a 1% yield of polymer after 45 min at 100 °C. An analogous reaction gave a yield of 24% when 10 equiv (relative to **1**) of 1-butanethiol was included as a chain transfer agent. A control reaction containing the thiol but lacking **1** gave only a 1% yield of polymer, thus confirming that the dramatic increase in polymerization rate was due to the chain transfer reaction of the thiol rather than independent initiation by the thiol. In typical monoradical polymerizations, addition of chain transfer agents only slightly affects the rate of polymerization, so the chain transfer agent's dramatic effect on the rate of polymerization in this system is evidence in support of the diradical mechanism predicted by theory.

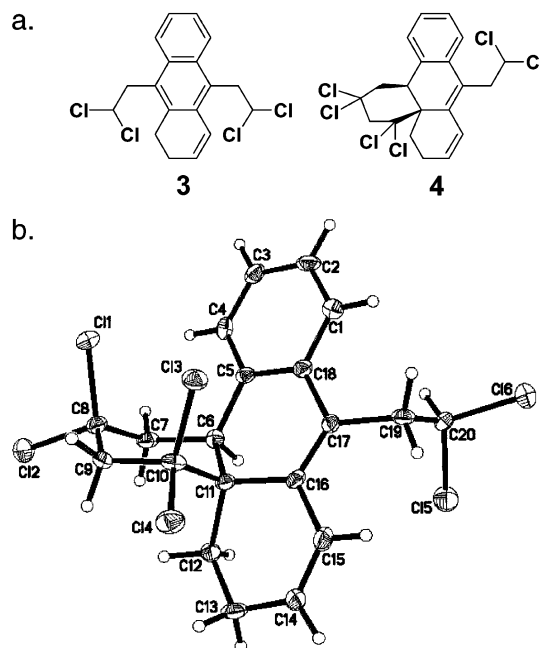


Figure 2. (a) Small molecule byproducts of diradical-initiated polymerization of VC. (b) ORTEP drawing depicting trimer **4**.

We have demonstrated the successful initiation of addition polymerizations by the diradical resulting from Bergman cyclization, and we have shown that the behavior of this diradical initiator is in agreement with theory. By exploiting the dependence of the Bergman cyclization on the geometry of the enediyne substrates, new triggers for radical polymerization based on strain-induced reactivity could potentially be developed. These studies are now in progress.

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Supporting Information Available: GPC, FD-MS, and UV absorption data for oligomeric MMA, experimental procedures and characterizations, control polymerization data, calculations of C_1 , and crystallographic data for **4** (PDF and CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

References

- (1) Haward, R. N. *Trans. Faraday Soc.* **1950**, *46*, 204–210.
- (2) Zimm, B. H.; Bragg, J. K. *J. Polym. Sci.* **1952**, *9*, 476–478.
- (3) Johnson, D. H.; Tobolsky, A. V. *J. Am. Chem. Soc.* **1952**, *74*, 938–943.
- (4) Borsig, E.; Vadnalova, O.; Kolar, P.; Lazar, M. *Chem. Zvesti.* **1976**, *30*, 328–335.
- (5) Li, T.; Willis, T. J.; Padias, A. B.; Hall, H. K. *Macromolecules* **1991**, *24*, 2485–2487.
- (6) Toplikar, E. G.; Herman, M. S.; Padias, A. B.; Hall, H. K.; Priddy, D. B. *Polym. Bull.* **1997**, *39*, 37–43.
- (7) Wang, K. K. *Chem. Rev.* **1996**, *96*, 207–222.
- (8) John, J. A.; Tour, J. M. *J. Am. Chem. Soc.* **1994**, *116*, 5011–5012.
- (9) Drumright, R. E.; Terbrueggen, R. H.; Priddy, D. B.; Koster, R. A. U.S. Patent 5,618,900, April 8, 1997.
- (10) Semmelhack, M. F.; Neu, T.; Foubelo, F. *Tetrahedron Lett.* **1992**, *33*, 3277–3280.
- (11) Brandup, J.; Immergut, E. H.; Grulke, E. *Polymer Handbook*, 4th ed.; Wiley: New York, 1999.

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