Boron-Doped $C_{24}$ Fullerenes for Alkyl Functionalization or Potential Polymerization

M. Owen Hurst, Jr.,* Michael O. Hurst, Sr.,* and Ryan C. Fortenberry*✉

Department of Chemistry & Biochemistry, Georgia Southern University, Statesboro, Georgia 30460, United States

**ABSTRACT:** Replacing a single carbon atom in $C_{24}$ with a boron atom allows the functionalization of one additional carbon atom. Such a process involves little energy cost with regard to the structure of the fullerene. Two such replacements are required if the fullerenes are to act as "pearls on a string". This work shows trends for increasingly higher levels of carbon replacement with boron as well as hydrogenation, methylation, and ethylation of a subsequent carbon atom in such a boron-doped small fullerene. Additionally, dimers are shown to be stable, and the linking ethyl groups actually stabilize the overall structure more than when the ethyl groups are on the surface of the structure and are not serving as linkers. Such stringed fullerenes would certainly have applications to materials science if polymers could be made from these stringed pearls and would be suitable for neutron radiation shielding in spacecraft or spacesuits.

**INTRODUCTION**

The inherent stability of fullerenes makes them difficult to functionalize. Although there exists rich fullerene chemistry, most functionalization of these compounds comes from adding a cyclic group such as diepoxide or pyrrolidine over a $C\equiv C$ moiety within the structure.1−4 This disrupts the overall π cloud, resulting in a destabilization of the system. While such functionalization can have varied applications, even in the creation of veritable molecular submarines for delivering atomic cargoes for medical applications,5 other means of allowing buckyballs to bond to other species could have wide-ranging applications, opening up these molecules to more of their potential uses across the chemical spectrum.

Although the pure carbon forms of buckyballs are known for their stability, replacing each $C_2$ group with a $B\equiv N$ has been proposed and experimentally known almost since the beginning of fullerene chemistry in the 1980s.6−11 Although such cages have more desirable macroscopic properties such as melting points or sheer strength than their pure carbon cousins,12−15 the stability of the individual cages at the molecular level, that is, the average of the bond strengths, is actually weaker in the boron nitride fullerenes or nanotubes. The dative-type noncovalent interactions between the separate molecules make for more desirable mechanical properties, but the individual boron nitride structures are easier to break.

Recent work has shown that replacing up to half of the nitrogen atoms in $B_{12}N_{12}$ or $B_{16}N_{16}$ with a methylidyne (CH) actually stabilizes the structure.16−18 Most notably, when every four-membered ring contains a CH in place of a N and no six-membered rings contain more than one CH in place of a N, the fullerenes have higher average bond energies. Additionally, the presence of CH groups allows the direct functionalization of fullerenes to atoms that are already within the cage structure. Although there exists repulsion and a subsequent energy cost for the inclusion of alkyl groups onto the carbon formerly of the methylidyynes, adding more CH groups in a typical pattern will continue to stabilize the cage. As a result, polymers of CH-doped boron nitride fullerenes are possible with the fullerenes contained within the polymer and not as functional groups themselves, as has typically been proposed for fullerene-containing polymers.

This work extends these analyses to more pure fullerenes that are more desirable from synthetic and analytical perspectives. Fullerenes with a few doped inclusions in the cage structure have been known for some time,20−22 making them more likely to be analyzed experimentally.23 Buckyballs are known to have magic numbers of stability, with $C_{24}$ being one of the smallest of the allotropes.24,25 $C_{24}$ is isoelectronic with $B_{12}N_{12}$26 and it will be used as the prototypical fullerene for this study. A similar boron (and nitrogen) doping study on $C_{20}$ has shown that boron inclusion in the carbon cage can have a stabilizing effect27 as well as boron doping on graphene surfaces,28 but subsequent hydrogenation or alkylation has not been robustly explored in this regard.

Different from the previous work for B−N inclusion in $C_{24}$, the doping will instead be with the isoelectronic B−CH replacement of a $C_2$ group within the carbon cage. From another perspective, replacing a carbon atom with a boron atom opens one of the adjacent carbons to functionalization. Most readily, it will be a hydrogen atom. Hence, such inclusions will begin with the various isomers of $C_{24}$BCH and will build up to higher doping levels and/or alkyl functionalization instead of mere hydrogenation. Possible applications of this work include not only the synthesis of any such polymers but also, most...
notably, radiation shielding for spacecraft, components, and even humans above the low Earth orbit. Hydrogen shields primary neutron and cosmic ray radiation, whereas $^{10}$B shields secondary effects. Hence, durable materials that contain high amounts of boron and hydrogen could aid in both manned and unmanned space exploration. Polymers containing boron-doped fullerenes would fit this application nicely. This present study focuses on whether such structures are stable or not and will leave possible studies for polymerization and synthesis for future work.

### COMPUTATIONAL DETAILS

Geometry optimizations with density-fitted Møller–Plesset second-order perturbation theory (DF-MP2)\(^{29,30}\) are utilized for this study, combined with the 6-31+G* basis set\(^{31}\) within the PSI4 suite of quantum chemistry programs.\(^{32}\) The performance of DF-MP2 is quite efficient, opening up larger chemical systems to wave function analysis, making these computations ab initio unlike many popular flavors of density functional theory. Additionally, double-zeta MP2 is known to be notably accurate because of the fortuitous but nonempirical cancellation of errors.\(^{33-36}\)

The average bond, total molecular dissociation, binding, or, equivalently, stabilization energy ($E_s$) is defined from ref \(^{17}\) as

$$E_s = E_m - \sum E_a$$  \hspace{1cm} (1)

The $E_m$ value corresponds to the MP2/6-31+G* energy of the total molecule in the singlet ground state, and the MP2/6-31+G* $E_a$ values are the energies for each of the atoms or constituent molecular fragments. These include the lowest energy electronic configurations of B(2P) and C(3P), C(3P), 2H CH, 2$\text{A}'$ C=CH$_2$, 2A' C=CH$_2$CH$_3$ and 3$\text{A}_2$ C=CH$_2$CH$_{2}$=C, similar to that in ref \(^{17}\). In such a way, the $E_a$ are not biased for further bond dissociation because the only bonds broken are those within the cage molecule.

### RESULTS AND DISCUSSION

The DF-MP2/6-31+G-optimized structure of one isomer of C$_{22}$BCH is given in Figure 1. This particular structure is the easiest to conceive because any carbon atom on the cage is replaced by a boron atom, with the adjacent carbon atom, a different four-membered ring, having been hydrogenated. Alternatively, this isomer can be described as a C$_2$ group lying along an edge of two six-membered rings being replaced because boron and methylidyne are found on separate four-membered rings. To test if this isomer is of the lowest energy form, the other symmetry-unique isomers must be computed and their relative energies must be compared.

The nomenclature scheme for the replacement follows a fashion similar to those of refs \(^{17}\) and \(^{18}\). For the C$_{24}$ boron replacement and hydrogenation/alkylation, Figure 2 is most readily used, with the structure of C$_{23}$B expanded into a Schlegel diagram. The first boron replacement of a carbon is the reference point for all further isomerization analyses, and the numbered positions in Figure 2 showcase how each carbon atom is affected, either through boron replacement or functionalization. For the $n=1$ level, where $n$ is the number of C$_2$ moieties replaced, only the hydrogen atoms change their locations. For $n>2$, the markers to the left of the dash given in the isomer names, especially for Table 1, are for the second and higher boron atom replacements and are marked as “B”. The markers to the right of the dash are for the hydrogenated carbons (H), methylated carbons (M), and ethylated carbons (E). Upon dimerization, the E can also indicate where the ethyl linking group originates, and the two parentheses describe the replacement positions on each buckyball monomer unit.

**Monomers.** The $n=2$ isomers present a pattern that is both unsurprising and yet still unexpected. Most notably, for the former case, the 1H isomer has the lowest total $E_s$ as shown in Table 1. Negative numbers here indicate that the cage is preferred over the constituent atomic CH, CCH$_3$, or CCCH$_3$ pieces that make up the cage. However, unlike the CH replacements of B$_{12}$N$_{12}$, the overall $E_s$ is actually greater than that of C$_{24}$. It increases by 0.30 eV, but the total $E_s$ for C$_{24}$ is many orders of magnitude larger at $-151.71$ eV. Hence, replacement of a C$_4$ with B−CH in the cage destabilizes the cage only by a small amount. Furthermore, the most stable way to functionalize a C$_{24}$ after boron replacement is to create the structure given in Figure 1. From this geometry, it is clear that some puckering of the structure takes place because of a lack of p electrons on that atom. This is consistent with the previous boron nitride fullerene studies. Here, however, such puckering is destabilizing.

Figure 1. Optimized structure of C$_{22}$BCH in its 1H isomer.

Figure 2. C$_{23}$BCH reference structure as a Schlegel diagram (boron is shown in blue).
Table 1. Total and Relative Stabilization Energies ($E_s$ in eV) of the C$_{24}$ B–CH-Substituted Fullerene Isomers for $n$ Replacements of C$_2$ Groups

| $n$  | isomer                  | $E_s$ (total) | $E_s$ (rel.) |
|------|-------------------------|--------------|--------------|
| 0    | C$_{24}$                | -151.71      | 0.00         |
| 1    | 1H                      | -151.41      | 0.30         |
| 1    | 7bH                     | -151.32      | 0.39         |
| 1    | 5H                      | -151.19      | 0.52         |
| 1    | 3H                      | -151.14      | 0.57         |
| 1    | 9H                      | -151.01      | 0.70         |
| 1    | 1bH                     | -150.94      | 0.77         |
| 1    | 6H                      | -150.91      | 0.80         |
| 1    | 7H                      | -150.91      | 0.80         |
| 1    | 4bH                     | -150.80      | 0.91         |
| 1    | 2H                      | -150.60      | 1.11         |
| 1    | 8H                      | -150.58      | 1.14         |
| 2    | 2b-3H                   | -151.07      | 0.64         |
| 2    | 4b-9H                   | -151.07      | 0.64         |
| 2    | 3b-4H                   | -151.06      | 0.65         |
| 2    | 1bB-10bH                | -150.77      | 0.94         |
| 2    | 4bB-9bH                 | -150.76      | 0.95         |
| 2    | 6b-5H                   | -150.76      | 0.95         |
| 2    | 5b-6H                   | -150.68      | 1.03         |
| 2    | 9bB-8bH                 | -150.62      | 1.09         |
| 2    | 4b-3H                   | -150.61      | 1.10         |
| 2    | 5b-4H                   | -150.60      | 1.11         |
| 2    | 5b-6bH                  | -150.60      | 1.11         |
| 2    | 4bB-5H                  | -150.55      | 1.16         |
| 2    | 3b-4bH                  | -150.51      | 1.20         |
| 2    | 7bB-8bH                 | -150.50      | 1.21         |
| 2    | 4b-5H                   | -150.42      | 1.29         |
| 2    | 6B-7H                   | -150.36      | 1.36         |
| 2    | 6bB-3H                  | -150.34      | 1.37         |
| 2    | 7bB-6H                  | -150.19      | 1.52         |
| 2    | 9bB-10bH                | -150.16      | 1.55         |
| 2    | 8bB-10bH                | -150.11      | 1.60         |
| 2    | 8bB-9bH                 | -150.06      | 1.66         |
| 2    | 7B-6H                   | -150.03      | 1.68         |
| 2    | 7b-8H                   | -149.82      | 1.89         |
| 2    | 6B-7bH                  | -149.81      | 1.90         |
| 2    | 2B-18H                  | -149.74      | 1.97         |
| 2    | 7B-7bH                  | -149.66      | 2.05         |
| 2    | 1bB-2H                  | -149.53      | 2.18         |
| 3    | 2bB,3b-9,9H             | -149.77      | 1.94         |
| 3    | 6,10bB-5,12bH           | -149.74      | 1.97         |
| 3    | 2,7bB-1b,7H             | -149.12      | 2.60         |
| 3    | 1b,6B-2,7bH             | -148.85      | 2.86         |
| 3    | 1b,7B-2,7bH             | -148.51      | 3.20         |
| 3    | 2,6b,1b,7H              | -148.19      | 3.52         |
| 4    | 4,7b,10bB-8b,9,12bH     | -149.20      | 2.51         |
| 4    | 2,4,1bB-3,9,12H         | -148.56      | 3.15         |
| 5    | 2.4,8bB,11bB-1b,3,9,12,10bH | -147.64 | 4.07       |
| 6    | 1b,4b,7b,8b,13B-2,5,9,11b,11,14H | -148.10 | 3.62 |
| 12   | B$_{12}$(CH)$_{12}$      | -140.27      | 11.44        |
| 1    | 1M                      | -150.94      | 0.77         |
| 2    | 4b-9M                   | -150.02      | 1.69         |
| 2    | 8bB-7M                  | -149.60      | 2.11         |
| 1    | 1E                      | -150.92      | 0.79         |
| 2    | 8bB-7E                  | -149.81      | 1.89         |

In any case, methylidene does not have to be created because of hydrogenation of an adjacent carbon. Hydrogenation at the 7b position is nearly favored with an $E_s$ of 0.39 eV above C$_{24}$. The 7bH-C$_{22}$BCH has the hydrogen on the carbon atom diametrically opposed to the boron atom. The 5H isomer is the next-lowest, followed by the 3H isomer. Of all $n = 1$ isomers, the 2H and 8H isomers are the least favored, indicating that near and far methylidenes are favored over an intermediate distance to the reference boron atom. The reason for this likely results from the bonding and nonbonding highest occupied molecular orbital (HOMO) patterns, shown in Figure 3, of 1H-C$_{25}$BCH. The stable positions have the methylidene groups in nonbonding portions of the HOMO while inclusion of the CH groups in π lobes disrupts the overall MO structure to a greater degree. In any case, replacement of a carbon atom with a boron atom and a subsequent hydrogenation of another carbon atom somewhere on the cage will destabilize the structure by less than 1.15 eV which is still less than 1.0%. All higher $n$ level monomers analyzed here will assume that the first carbon hydrogenated will be in the 1 position. Hence, the nomenclature will not expressly describe the first carbon hydrogenation.

Moving to the $n = 2$ level actually brings a surprise. The most stable isomers actually have the boron atoms substituted onto the same six-membered ring as the reference boron at the 2, 4, and 3 positions. Additionally, the 1H position of the methylidene is also found in this ring. Furthermore, the corresponding second hydrogenation to create the second methylidenes in the cage also occurs in this same ring at the 3, 9, and 4 positions, as given in Table 1. As a result, 0.65 eV is the minimum energy increase for double boron replacement/hydrogenation, which takes place within the same ring. The response may be in such a way that one ring is already perturbed and that a low energy cost is involved to boronate the cage, which disturbs the same six-membered ring as opposed to disrupting one of the other seven. However, the 4B-3H-C$_{20}$B$_2$(CH)$_2$ isomer at 1.10 eV has a relative $E_s$ nearly double that of the 3B-4H isomer at 0.65 eV. Although this difference is not significant in the scheme of the total $E_s$ it showcases that placement does matter because the second boron and hydrogenated carbon are within the same four-membered ring. This is disfavored here because a regular carbon atom separates the two B–CH groups, causing interference. As a result, the boron atom replacements are not favored on opposite (para) positions of a six-membered ring but are more favored at meta positions on the ring.

All of the symmetry-unique isomers for the replacement of a second boron atom and an adjacent carbon hydrogenation are
tested here. The range of energies for \( n = 2 \) stretches from this 0.65 eV level all the way up to 2.18 eV. As a result, replacing carbon atoms with the second boron and its corresponding hydrogenation of another carbon atom raise the energy by roughly one additional electronvolt. Putting the boron atoms on the opposite side of the cage from one another is not favored. However, the least favored reactions have two replacements, either of a boron or a methylidene, on one four-membered ring. Again, although the total increase in \( E_s \) is not seemingly prohibitive, some cages are more stable than the others. As the \( n \) level increases, this becomes more marked.

The most stable \( n = 3 \) isomer tested is the 2,4B-3,9H-C\(_{18}\)B\(_3\)(CH)\(_3\) form, where one of the eight six-membered rings is fully replaced in an alternating B–CH pattern around the ring, with a relative \( E_s \) of 1.94 eV, given in Table 1. This is a notable increase over the lowest \( n = 3 \) isomer but less than the highest \( n = 2 \) isomer. Although modeling all of the \( n = 3 \) isomers is intractable, trends begin to emerge. The next-lowest \( n = 3 \) isomer tested has nearly the same \( E_s \) at 1.97 eV, but the boron atoms are as far away from one another as possible. The newly hydrogenated carbon atoms are still adjacent to their corresponding boron atoms. However, they continue to be in different four-membered rings. Replacement of more than two atoms, either B or CH, in a single four-membered ring destabilizes the structure to a greater extent.

On the whole, inclusion of a third boron atom and a hydrogenated carbon atom raise \( E_s \) by roughly another whole electronvolt. For two \( n = 4 \) isomers, \( E_s \) continues to rise but can vary depending upon the location of the boron atoms and hydrogenated carbons. This trend endures for \( n = 5 \), as shown at the bottom of Table 1. The chosen token \( n = 6 \) isomer, 1b,4b,7b,8b,13b-2,5,9,110b,11,14H, has one B–CH in every four-membered ring, which is why its \( E_s \) value (3.62 eV) is less than that of the token \( n = 5 \) isomer (4.07 eV). Regardless, full replacement at the \( n = 12 \) level results in an 11.44 eV \( E_s \) relative to C\(_{24}\). As such, the \( n \geq 7 \) levels will grow \( E_s \) at a faster rate because more than two atoms will have to be replaced in each four-membered ring. Hence, functionalization of C\(_{24}\) through B–CH doping is likely best done with as few replacements as possible.

To see how functionalization can take place, methylation, as opposed to hydrogenation, of the carbon atoms to create :C–CH\(_3\) groups will now be present within the cage. These so-called M groups here showcase how further interference with the cage takes place with bulkier groups. The bottom of Table 1 shows their \( E_s \) values. Putting an M group at the 1 position for the 1M isomer only has a cost of 0.77 eV. Although this is double that of hydrogenation, it is still less than that of the more costly \( n = 1 \) CH-containing isomers. Moving up to \( n = 2 \) for the M isomers increases \( E_s \) by roughly 1.0 eV once more. Having the second B atom and M group at the most favorable positions from the hydrogenations to produce the 4B-9M-C\(_{20}\)B\(_2\)CHCCH\(_3\) isomer is much more favored at a relative \( E_s \) of 1.69 eV than by putting the additional boron and M group on the diametric opposite side of the cage with an energy increase of 2.11 eV. Further functionalization with more boron atoms and carbon methylation will certainly destabilize the cage further, as was shown for the higher \( n \) levels for the hydrogenation.

Moving from the M to the E groups, where the latter is precisely a :C–CH\(_3\)CH\(_3\) group within the cage, shows that there is little difference between M and E. For instance, a single B replacement and carbon atom ethylation at the \( n = 1 \) level produce nearly the same \( E_s \) as a methylation. The 1E \( E_s \) relative to C\(_{24}\) is 0.79 eV, merely 0.02 eV more than the 1M three rows above in Table 1. The terminal hydrogens in the alkyl ethyl group interact with the \( \pi \) electrons on the surface of the cage, stabilizing the functional group nearly as much as the hydrogen atoms on the first carbon atom in the ethyl group repel one another. This stabilization of the ethyl group is further evidenced in the \( n = 2 \) E level because the 8bB-7E isomer is actually 0.22 eV lower than the 8bB-7M isomer. Hence, adding methyl or ethyl groups to the outside of the cage will destabilize the structure a little, but ethyl group additions will not cause large disturbances in the cage structure, allowing for linkage between monomers.

**Ethyl-Linked Dimers.** To analyze the possible polymerization of these boron-doped fullerenes, dimers are constructed here and tested to see how well the monomers may attach to one another. To analyze how C\(_{24}\)B cages can alkylate, the lowest energy isomers of the hydrogenated monomers are constructed in joint pairs with their \( E_s \) values now relative to 2-C\(_{24}\) monomers. As a first case, the (7bE)(5E) dimer isomer (also shown visually in Figure 4) has an increase of \( E_s \) of only 1.02 eV upon boron replacement and ethylation. Looking at combinations from the other lowest monohydrogenated isomers of the 1 and 3 positions, in addition to the 3 and 7 positions, produces \( E_s \) values only slightly above this value, ranging up to 1.31 eV for the studied isomers. This is less than 0.5% destabilization of the total fullerene cage.

The trend is quite clear from the present structures that alklylation and dimerization may even be less costly per monomer than for the monomer alone as the \( E_s \) values in Table 2 highlight. For instance, ethylation on the

![Figure 4. Optimized structure of (7bE)(5E)-2C\(_{24}\)BE.](image)

**Table 2. Total and Relative Stabilization Energies (\( E_s \) in eV) of the Ethyl-Linked Fullerene Dimer Isomers**

| \( n \) (per cage) | isomer                  | \( 2C_{24} \) Rel. \( E_s \) |
|-------------------|------------------------|-------------------------------|
| 1                 | (7bE)(3E)              | −302.41                       | 1.02                          |
| 2                 | (7bE)(5E)              | −302.30                       | 1.13                          |
| 3                 | (1E)(3E)               | −302.28                       | 1.15                          |
| 4                 | (1E)(5E)               | −302.18                       | 1.25                          |
| 5                 | (1E)(7E)               | −302.14                       | 1.28                          |
| 6                 | (12E)(11H)(12bB-8H,11E)| −302.11                       | 1.31                          |
| 7                 | (12bB-7E,11H)(12bB-5H,11E)| −302.28                     | 3.14                          |
| 8                 | (12bB-7E,11H)(12bB-3H,11E)| −302.00                     | 3.20                          |
| 9                 | (12bB-7E,11H)(12bB-5H,11E)| −302.06                     | 3.37                          |
| 10                | (12bB-5E,11H)(12bB-3H,11E)| −299.93                     | 3.50                          |
| 11                | (8bE-1E,7bH)(13bB-12bH,5E)| −297.76                     | 3.67                          |
| 12                | (5b-7E,4H)(10bB-3E,12bH)| −296.63                      | 3.80                          |
| 13                | (12bB-7E,11M)(12bB-5M,11E)| −297.39                     | 4.03                          |
| 14                | (12bB-1E,11M)(12bB-3M,11E)| −299.04                     | 4.38                          |
monomer has an $E_2$ of 0.79 eV at the 1 position. The (1E)(3E) dimer isomer has an $E_2$ of 1.15 eV. Half of that is 0.58 eV, which is less than 0.79 eV. Hence, alkylation of the boron-doped cages is promising.

However, at least double substitutions for the $n = 2$ level per cage have to be stable because any polymer would require alkylation to at least two sites on each cage to continue the polymer. Ethylation to link the monomers followed by hydrogenation to showcase that such double replacements per cage are possible for the dimer is also given in Table 2. In these cases, the first boron atom position is not named because it is the reference point. Again, putting boron atoms and corresponding hydrogenated carbons on opposite sides of the fullerene cage is not the most favored interaction. Instead, this falls to meta-type structures where the opposing functionalized carbon atoms are roughly 2/3 of the way around the cage from one another. Although these are stable, questions with regard to the former case is the more stable, but in di.

Methylating the two lowest energy $n = 2$ dimer hydrogenated isomers also adds roughly another electronvolt of cage destabilization. However, this is essential if these “pearls” can be strung together. The relative energy cost is about 1.5%, but such small destabilizations are likely readily absorbed by the cages. Ethylation instead of methylation as well as having the additional fullerenes to interact with the hydrogen atoms in the alkyl linkers will likely reduce this energy cost, as has been shown for the monomers and the $n = 1$ dimers. Hence, the destabilization per cage will likely average down to 1.0%, an almost certainly acceptable value.

Higher levels of boron replacement and corresponding alkylation will increase the energy cost. As such, the $n = 2$ replacement level is almost certainly the highest desired value. This is enough to provide the fullerenes with the capability to form chains and rings similar to the allotropes of sulfur. Such structures could have applications across materials science for flexible electronics, strong materials, and radiation shielding.

**CONCLUSIONS**

If two boron atoms can be introduced into C24 cages, then two carbon atoms can be functionalized. After functionalization, these cages can be linked together potentially to form polymers. Although such processes do introduce an energy cost, the trends shown here infer that this cost will be less than 1% of the total $E_2$. This energy cost is low enough that the cages should be able to absorb this slight destabilization, with little effect on the structures. Such single- or double-boron doping should be experimentally practical and is more promising than methylidene replacement in boron nitride fullerenes.

Specifically, for this study, replacing a carbon atom with a boron atom and hydrogenating or otherwise alkylling a second carbon atom in a C24 fullerene destabilize the cage but by less than 1%. The replacing boron atoms and their alkylated carbon atom counterparts are most stable and adjacent to one another but in different four-membered rings. However, the second and higher boron atoms prefer to be either in the same six-membered ring or in a position close to but not quite opposite from one another. Although the former case is the more stable, the latter case is close to $E_2$ and will likely be necessary for any polymerization.

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