nature portfolio

Peer Review File

1,1-Polymerization of Acetylene

Corresponding Author: Professor Shifa Zhu

This file contains all reviewer reports in order by version, followed by all author rebuttals in order by version.

Version 0:

Reviewer comments:

Reviewer #1

(Remarks to the Author)
The revised manuscript is significantly improved. I recommend publication.
I still think this paper brings creative chemistry of the highest novelty. Congratulations.
minor issues: 1) It seems more appropriate to describe the structure as "branched" than "brush". according to Sherburn et al :"Dendralenes are the acyclic, branched class of structures that..." in Chem. Sci.,2019, 10, 9969.
Brush in polymer science refers to much longer side chains.
2) in the SI a space should be insert between a number and a unit

Reviewer #2

(Remarks to the Author)
I have reviewed a previous submission of this manuscript to Nature Synthesis, and my main concern was the lack of broad appeal of the work. I think Nature Communications is a more appropriate venue for this work. The authors addressed my other critiques regarding the manuscript, and my issue is now primarily with the supplementary information, which is still not formatted properly. The authors need to do the following:
(1) Every figure (including spectra) should be numbered (Fig. S1, Fig. S2, etc.) and captioned, and there should only be a single figure per page.
(2) xyz coordinate files should be provided for the computed structures
(3) In one of the procedures, the authors say about handling hexafluoroacetylacetone, "...stop breathing while weighting! (sic)." This sort of advice is NOT standard procedure and should not be present in a manuscript. The standard procedure is to carry out all operations in a functioning fume hood.
(4) Also, the authors should comment and emphasize the level of contact that can trigger explosions of their IPA: is a touch with a spatula enough to detonate? Is using glassware with frits or ground-glass joints OK? Are screw-cap vials OK to use or is there danger of detonation from material ending up in the joint?
(5) Please use proper notations in the SI: for example, "3" should be a subscript in CDCl3, and 1 should be superscript in 1H NMR.

In addition, the authors should address a few issues in the main text:
(1) the authors should change "which was proposed to be due to postpolymerization or cross-linking" to "which was proposed to be due to post-polymerization cross-linking."
(2) Figure 5 should have section labels (A, B, C...), and those labels should then be incorporated in the caption.
(3) In the caption to Figure 3, the authors say "‡Differences in the hydroboration process exist"—what do the authors mean by "differences in hydroboration" exactly? Pointing the reader to the SI is fine for details, but this statement should be less ambiguous to begin with.

Once these issues are addressed, I'd be happy to recommend acceptance.

Reviewer #3

(Remarks to the Author)
In this revision, the majority of the comments have been adequately addressed. However, the second comment from

Reviewer 3 was ignored.
The authors should add the representative 1,1-addition polymerization Polyhomologation (J. Am. Chem. Soc. 1997, 119, 38, 9049–9050) in Figure 1, This will enable the audience to understand the background and emphasize the distinctive characteristics of 1,1-addition polymerization of acetylene.
This manuscript is recommended to be published in Nature Communication after minor revision.

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Brush in polymer science refers to much longer side chains.
2) in the SI a space should be insert between a number and a unit

Answer:

Thank you for your positive assessment of the revised manuscript and your recommendation for publication.

Regarding the naming of the polymer:

We appreciate your comment regarding the use of "branched" versus "brush-like" to describe the polymer structure and agree that "brush" typically implies much longer side chains in polymer science. However, another Reviewer strongly argued that "branched polymer" conventionally implies a structure with a backbone and side chains. They contended that the synthesized material is specifically polyacetylene formed via 1,1-addition mode facilitated by 1,1-carboboration, making the description "branched Polyacetylene" problematic. In order to solve this dilemma and to better reflect the specific 1,1-addition mechanism central to this work, we now adopted the term **"1,1-polyacetylene (1,1-PA)"** for the synthesized polymer. Consequently, the manuscript title has been revised to **"1,1-Polymerization of Acetylene"** to ensure consistency and clarity, avoiding the potential misunderstandings associated with both "branched" and "brush-like" in this specific context.

Regarding minor issues:

The suggested spaces between numbers and units have been inserted throughout the Supporting Information.

Thank you again for your valuable feedback, which has helped us improve the manuscript's precision.

Reviewer #2 (Remarks to the Author):

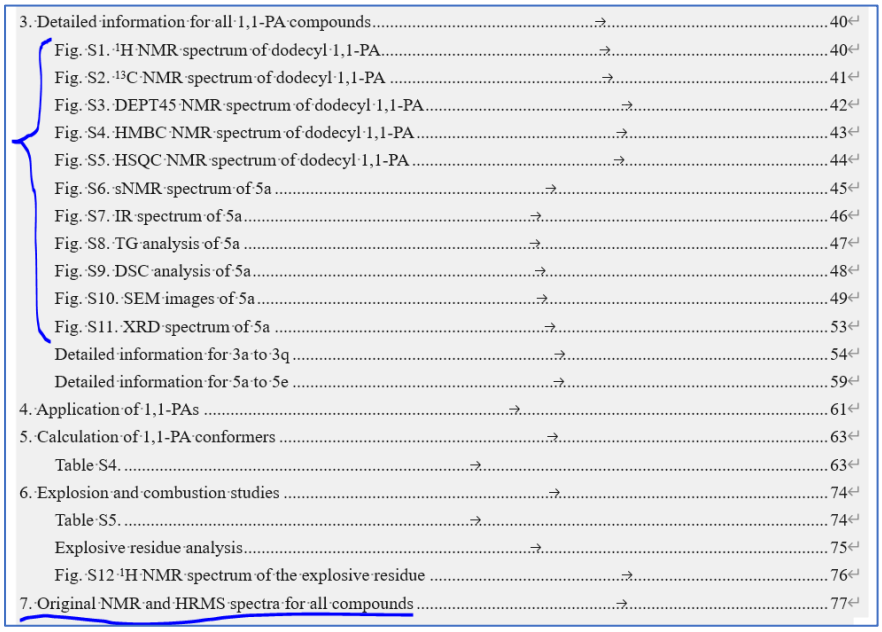
I have reviewed a previous submission of this manuscript to Nature Synthesis, and my main concern was the lack of broad appeal of the work. I think Nature Communications is a more appropriate venue for this work. The authors addressed my other critiques regarding the manuscript, and my issue is now primarily with the supplementary information, which is still not formatted properly. The authors need to do the following:

(1) Every figure (including spectra) should be numbered (Fig. S1, Fig. S2, etc.) and captioned, and there should only be a single figure per page.

Answer: In the updated Supplementary Information, **all figures directly cited in the main text have been clearly numbered and captioned within the SI.**

Regarding spectra not directly cited or discussed in the main text (such as raw NMR spectra and raw HRMS spectra), due to their large quantity and relatively lower importance, **we have consolidated them into a dedicated appendix section at the end of the latest SI version.** These spectra are organized sequentially by compound number (3a to 3q, 4a to 4b, 5a to 5e).

The vast majority of figures in the updated SI are now arranged according to the one figure per page requirement. The only exceptions are a small number of figures with an intrinsically strong correlation, such as SEM images showing sequential magnification of the same particle, which are grouped together.



(2) xyz coordinate files should be provided for the computed structures

Answer: The Cartesian coordinates are added

Cartesian coordinates for spiral conformer of [18]dendralene (Fig. 7 in the main text)

Symbol	X	Y	Z
C	8.6957769	0.8721740	-0.7157684
H	9.7854345	0.8902608	-0.7012333
C	8.0227693	2.0346379	-0.7493053
H	8.5434189	2.9867001	-0.7531066
H	6.9388691	2.0714252	-0.7850167
C	8.1007470	-0.4758873	-0.7287914

Cartesian coordinates for spiral conformer of [24]dendralene

Symbol	X	Y	Z
C	11.2023040	0.6596170	2.0167020
H	10.1190190	0.6384030	2.0779120
H	11.7230930	1.2270840	2.7810630
C	11.8744010	0.0065150	1.0538110
H	12.9636980	0.0422220	1.0492280

Cartesian coordinates for spiral-staircase conformer of [24]dendralene

Symbol	X	Y	Z
C	13.1821380	0.1795870	-1.6377450
H	12.2433030	0.1257540	-2.1797310
H	14.0874240	0.0183580	-2.2136970
C	13.2297260	0.4396760	-0.3203290
H	14.1985780	0.4942080	0.1759210
C	12.0719290	0.6850360	0.5574690

Cartesian coordinates for staircase conformer of [24]dendralene

Symbol	X	Y	Z
C	-13.3785700	-1.4465310	1.2056390
H	-12.4272960	-1.4874850	1.7265670
H	-14.1407080	-2.1487930	1.5269490
C	-13.6107220	-0.5683810	0.2157550
H	-14.5870300	-0.5597670	-0.2686330
C	-12.6598670	0.4366550	-0.2922510

(3) In one of the procedures, the authors say about handling hexafluoroacetylacetone, "...stop breathing while weighting! (sic)." This sort of advice is NOT standard procedure and should not be present in a manuscript. The

standard procedure is to carry out all operations in a functioning fume hood.
Answer: It has now been changed to a more standard procedure.

> 6) add 15 g (2.0 eq, 72 mmol) hexafluoroacetylacetone (**NOTE:** volatile poisonous and bad smiling liquid, must be weighted and operated in fume hood!)

(4) Also, the authors should comment and emphasize the level of contact that can trigger explosions of their lPA: is a touch with a spatula enough to detonate? Is using glassware with frits or ground-glass joints OK? Are screw-cap vials OK to use or is there danger of detonation from material ending up in the joint?
Answer: Thank you for raising this important safety concern. We had indeed included a safety disclosure in the previous version of the manuscript. In direct response to your query, we have comprehensively revised and significantly expanded the safety considerations in the current version.

(The following text is also presented in the Method section of the main article)

1. Long-chain 1,1-PA can be explosive. Appropriate personal protective equipment (PPE), including safety goggles, a certified respirator, gloves, and a lab coat, must be worn properly. Work should be conducted in a fume hood.
2. Reactor Safety: The heat released by the reaction causes a significant increase in internal pressure during polymerization. Therefore, the reactor vessel must be rated for a maximum operating pressure at least 20 times higher than the initial acetylene pressure to accommodate pressure surges and the high-pressure reactor must be equipped with a pressure relief valve.
3. Explosion Sensitivity of long-chain 1,1-PA:
    a) Critical Factor: The primary factor determining explosion risk is the age/freshness of the sample and its exposure to air, not the use of non-metal spatulas, ground-glass joints, or light exposure.
    b) Fresh Material (≤ 1 day old, especially immediately after filtration): Requires rigorous exclusion of air contact (e.g., via nitrogen purging or glovebox handling) to prevent self-oxidation. Heat accumulation from slow oxidation can sometimes trigger spontaneous explosion.
    c) Aged Material (> 1 day old) or Material Stored in a Glovebox: Exhibits substantially reduced explosion sensitivity. Standard handling procedures (e.g., using metal spatulas for weighing), excluding grinding, are generally safe.
4. Despite its high impact sensitivity, long-chain 1,1-PA possesses characteristics enabling safe handling with proper precautions:
    a) Low Ignition Temperature: Insufficient to ignite directly contacting materials like paper towels.
    b) Low Explosive Power: Insufficient to shatter non-sealed glass vials containing the sample. (This is only true for decomposition explosion. The oxidation explosion triggered by open flames is very violent.)
    c) Rapid Activity Loss: All documented accidental explosions occurred within 30 minutes of preparation.
5. Waste Disposal: Waste 1,1-PA should be diluted with silica gel or sand and disposed of as solid waste.
6. Comprehensive step-by-step operating procedures, including photographs, are provided in the SI to maximize safety.

(5) Please use proper notations in the SI: for example, "3" should be a subscript in CDCl3, and 1 should be superscript in 1H NMR.
Answer: They are all corrected in the new version

In addition, the authors should address a few issues in the main text:

(1) the authors should change "which was proposed to be due to postpolymerization or cross-linking" to "which was proposed to be due to post-polymerization cross-linking."

Answer: It has now been changed as you suggestion.

(2) Figure 5 should have section labels (A, B, C...), and those labels should then be incorporated in the caption.

Answer:

Before modification 👇

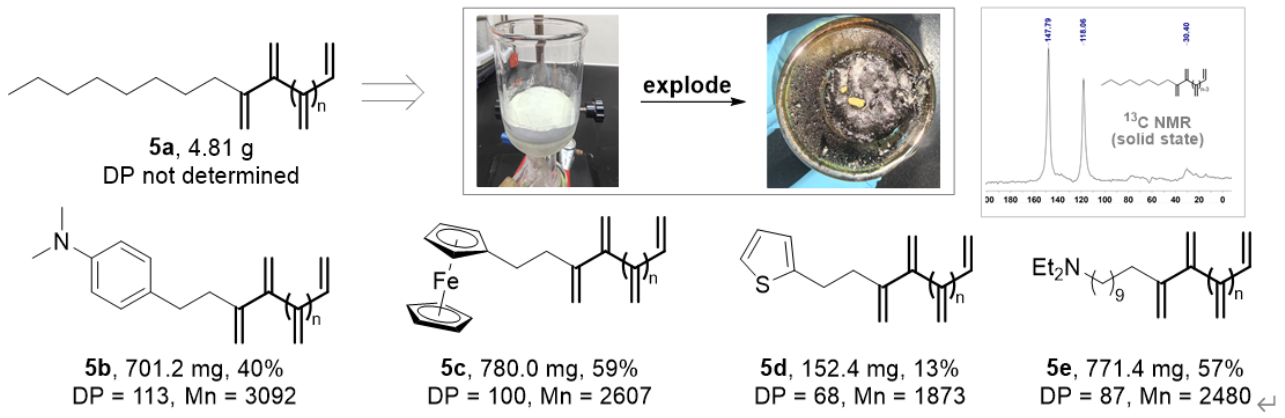
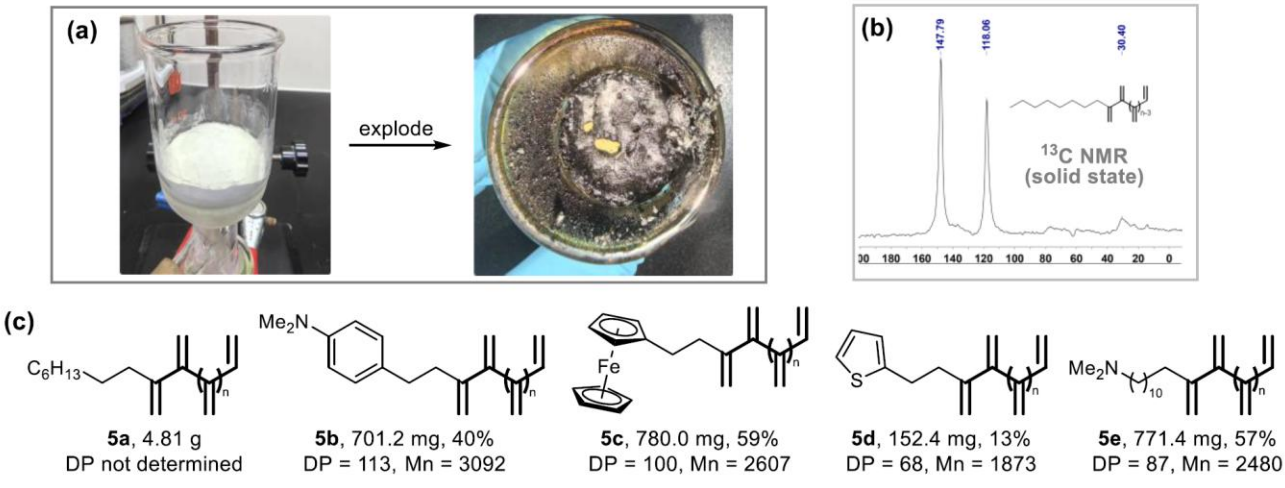


Fig. 5 Synthesis of long-chain bPAs. 5 mmol scale for **5a** and 0.5 mmol scale for others. DP determined by end group elemental analysis. Two photos of **5a** before and after explosion. Solid state ^{13}C NMR.

After modification 👇



(3) In the caption to Figure 3, the authors say "‡Differences in the hydroboration process exist"—what do the authors mean by "differences in hydroboration" exactly? Pointing the reader to the SI is fine for details, but this statement should be less ambiguous to begin with.

Answer: We specified the differences to non-standard stoichiometry/temperature/handling in the new version.

Fig. 3 Synthesis of short-chain 1,1-PAs. †Ph-BBN was synthesized from PhMgBr and Cl-BBN and was isolated before use. ‡Hydroboration conditions: non-standard stoichiometry/temperature/handling. See SI.

Once these issues are addressed, I'd be happy to recommend acceptance.

Reviewer #3 (Remarks to the Author):

In this revision, the majority of the comments have been adequately addressed. However, the second comment from Reviewer 3 was ignored.

The authors should add the representative 1,1-addition polymerization Polyhomologation (J. Am. Chem. Soc. 1997, 119, 38, 9049–9050) in Figure 1, This will enable the audience to understand the background and emphasize the distinctive characteristics of 1,1-addition polymerization of acetylene.

This manuscript is recommended to be published in Nature Communication after minor revision.

Answer:

We highly appreciate your positive assessment of our work and the previous revisions. We fully agree with your suggestion to present the seminal work on 1,1-polyhomologation (*J. Am. Chem. Soc.* **1997**, 119, 38, 9049-9050) in Figure 1. It has now been added and discussed in the Introduction. Thank you for your valuable suggestion.

The revised Figure 1 is enclosed bellow: