

Unsaturated Cyclic Lactam Polymers

By: Robert B. Login rloginconsulting.com

I have always learned new chemistry by studying and thinking up what I hoped were realistic ideas based on my understanding of the new (to me) chemistry. It was no fun to just understand the chemistry without thinking up new uses. I suppose this is typical of many scientists. As an industrial R&D chemist, you are limited by what your employer can do usually based on their chemistry. Ever since I retired, I have been free of those limitations. This has resulted in studying chemistry that I am interested in such as metathesis based polymerization (ROMP).

The first thing I found was the immense literature concerning this technology. With the help of Google Scholar, a fantastic resource, I started reading the ROMP literature.

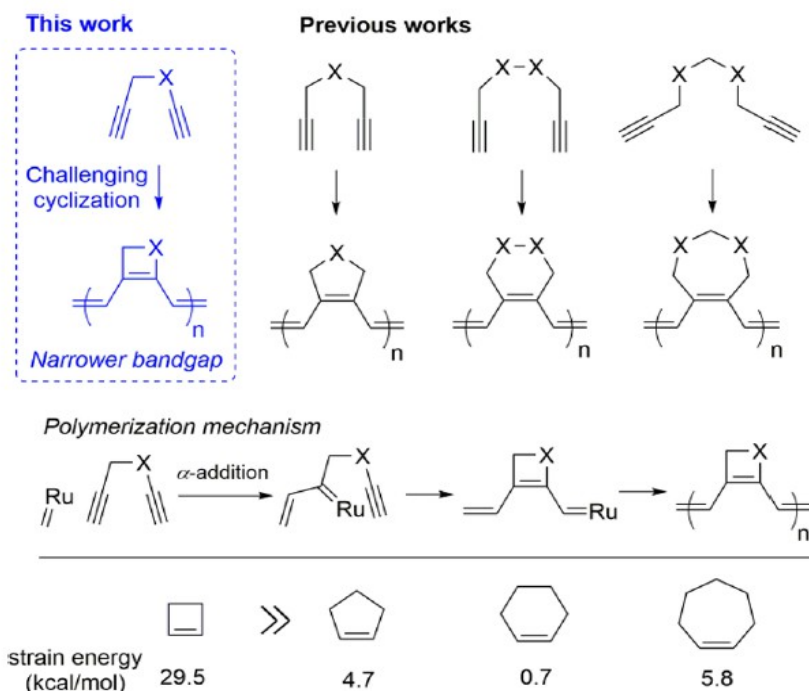
Cyclopolymerization of acetylene derivatives was one of the topics that appealed to me.

1,6-Heptadiyne and its homologues of substituted acetylenes are very interesting examples of substituted acetylenes, which can be susceptible to the ring-forming polymerization to give a new type of conjugated polymer backbone system. The present review deals with the comprehensive research results in the field of poly(1,6-heptadiyne)-based conjugated polymer chemistry.

Choi, S. K., Gal, Y. S., Jin, S. H., & Kim, H. K. (2000). Poly (1, 6-heptadiyne)-based materials by metathesis polymerization. *Chemical reviews*, 100(4), 1645-1682.

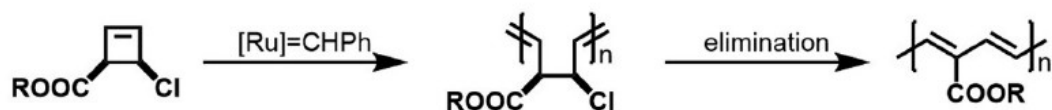
Kang, C., Kang, E. H., & Choi, T. L. (2017). Successful cyclopolymerization of 1, 6-heptadiynes using first-generation Grubbs catalyst twenty years after its invention: revealing a comprehensive picture of cyclopolymerization using Grubbs catalysts. *Macromolecules*, 50(8), 3153-3163.

Scheme 1. α -Selective Cyclopolymerization of α,ω -Diyne, and Strain Energies of Cycloalkenes Depending on Ring Size



Kang, C., Jung, K., Ahn, S., & Choi, T. L. (2020). Controlled cyclopolymerization of 1, 5-hexadiynes to give narrow band gap conjugated polyacetylenes containing highly strained cyclobutenes. *Journal of the American Chemical Society*, 142(40), 17140-17146.

This is an excellent reference well worth reading and studying! It led me once again to think of lactams as a potential version of this cyclopolymerization chemistry.



A variety of 3-substituted-4-halocyclobutenes originating from Dewar lactone (2-oxabicyclo[2.2.0]hex-5-en-3-one) were synthesized and polymerized using the Hoveyda–Grubbs 2nd generation catalyst. The polymerization reactions were found to proceed in a controlled manner, which provided a means to tune polymer molecular weight and to effect chain extensions. Treating the polymers with an organic base (e.g., triethylamine) facilitated elimination and afforded the corresponding substituted poly(acetylene)s which featured substituents on every four carbon atoms along the polymer backbone. The polymers were

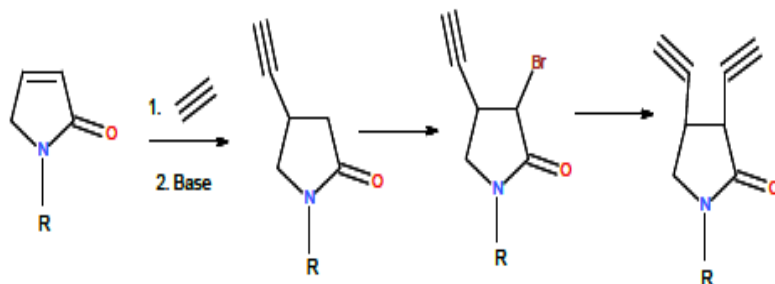
Abstract:

Seo, J., Lee, S. Y., & Bielawski, C. W. (2019). Dewar lactone as a modular platform to a new class of substituted poly (acetylene) s. *Polymer Chemistry*, 10(47), 6401-6412.

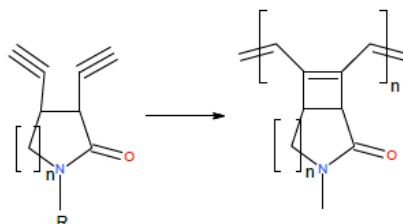
Perrott, M. G., & Novak, B. M. (1995). Living ring-opening metathesis polymerizations of 3, 4-difunctional cyclobutenes. *Macromolecules*, 28(9), 3492-3494.

Nistanaki, S. K., & Nelson, H. M. (2020). Dewar heterocycles as versatile monomers for ring-opening metathesis polymerization. *ACS Macro Letters*, 9(5), 731-735.

Why not marry this metathesis cyclopolymerization to lactams?

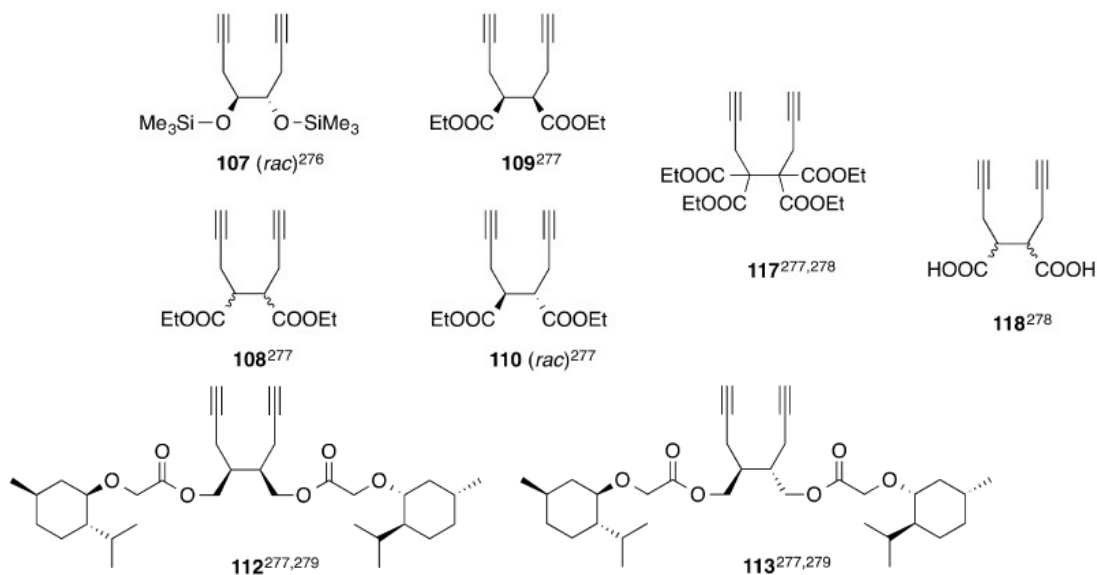


Scheme 1: Can this diacetylene pyrrolidone derivative undergo metathesis cyclopolymerization?



Scheme 2: I propose this cyclopolymerization.

Chart 6. Diynes Used in Cyclopolymerization Catalyzed by Schrock-Type Molybdenum and Tungsten Imido Alkylidene Complex Catalysts



I'm only showing monomers that have the acetylenic groups on two adjacent carbons from this reference.

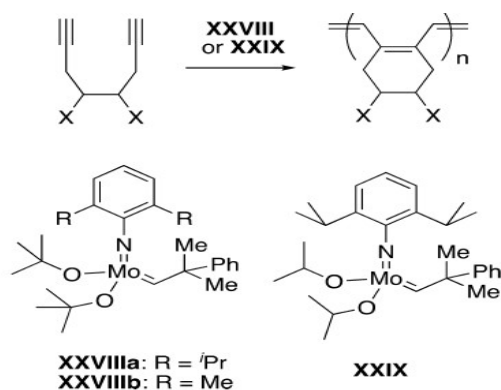


Figure 57. Stereoselective cyclopolymerization of 1,7-octadiynes.²⁷⁶

In this case the X's would be the lactam adjacent carbons.

Chart 8. 1,6-Heptadiynes Used in Cyclopolymerization by Grubbs Catalysts

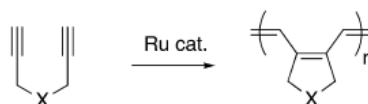


Chart 10. 1,7-Octadiynes Used in Cyclopolymerization by Grubbs Catalysts

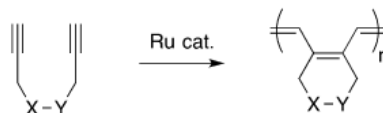
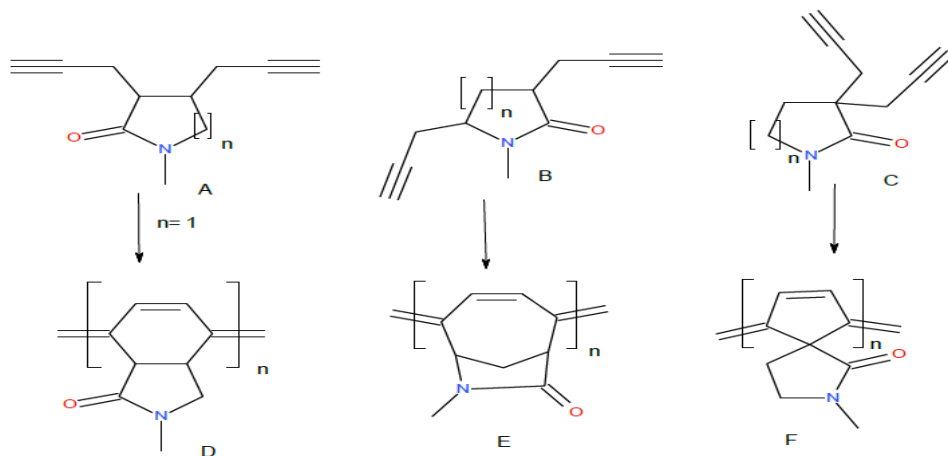


Chart 10 gave me hope that the X-Y could be part of cyclic structures but this review has no such examples. I think this review is very detailed so no mention of anything close to my proposals was worrisome. The above from:

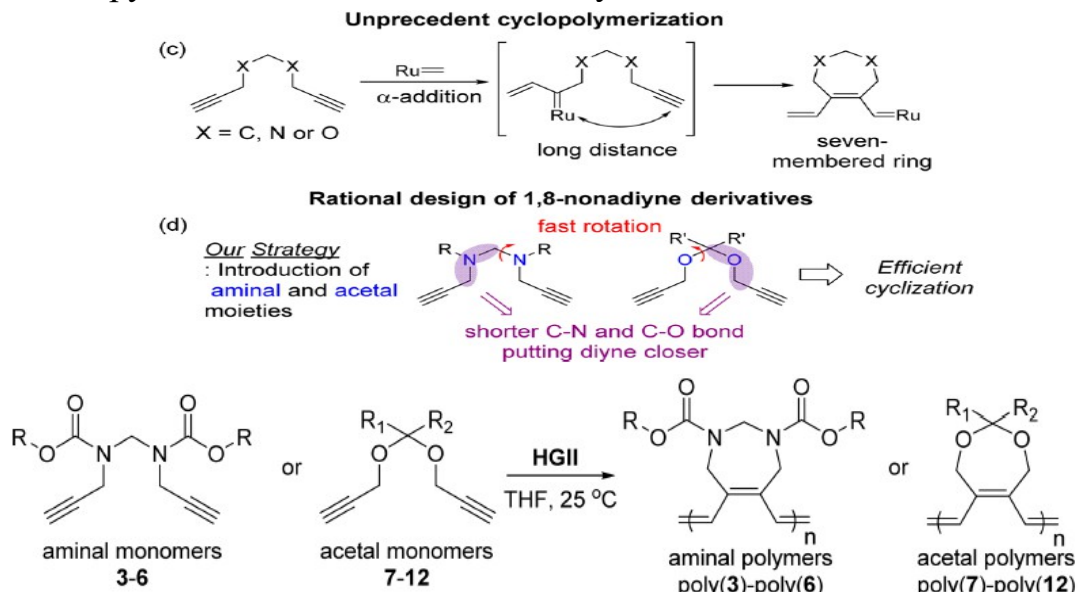
Pasini, D., & Takeuchi, D. (2018). Cyclopolymerizations: Synthetic tools for the precision synthesis of macromolecular architectures. *Chemical reviews*, 118(18), 8983-9057.

Choi, S. K., Gal, Y. S., Jin, S. H., & Kim, H. K. (2000). Poly (1, 6-heptadiyne)-based materials by metathesis polymerization. *Chemical reviews*, 100(4), 1645-1682.



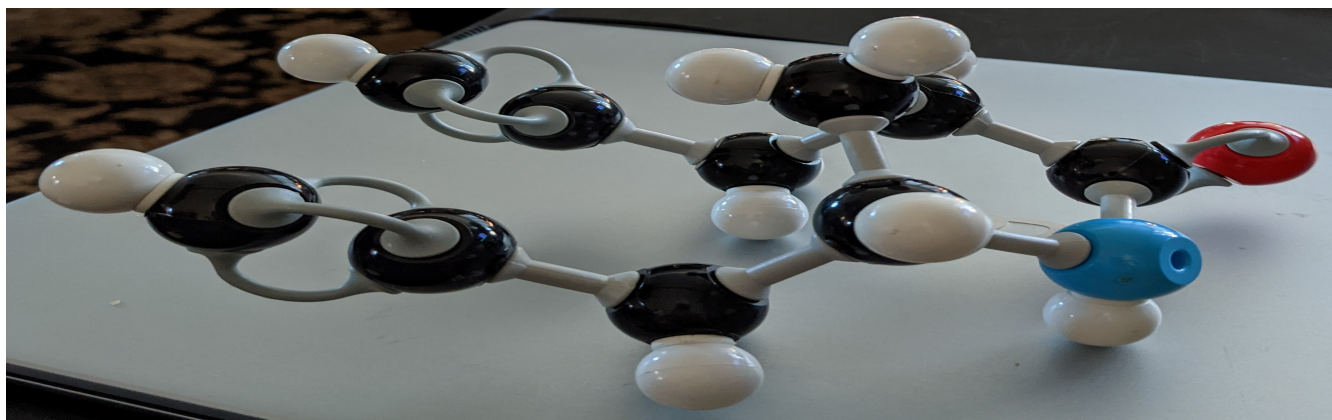
Scheme 3: The other possibilities. Here n=1 for B starting 2,4-pyrrolidone. D, E & F are

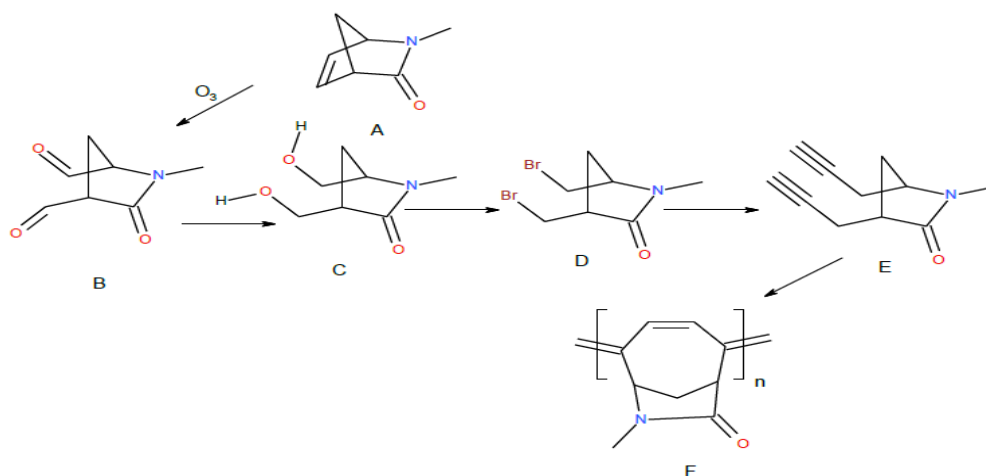
shown as the pyrrolidone derivatives for clarity.



Song, J. A., & Choi, T. L. (2017). Seven-membered ring-forming cyclopolymerization of 1,8-nonadiyne derivatives using Grubbs catalysts: rational design of monomers and insights into the mechanism for olefin metathesis polymerizations. *Macromolecules*, 50(7), 2724-2735.

This reference discovered the need for flexible and shorter bonds in these acetals and aminals in order to achieve high levels of CP 7-membered containing unsaturated polymers.





Scheme 4: The pictures above are views of E and show how close the triple bonds are to each other. Because of this closeness, I think that this proposal would work to produce F.

So why consider trying to synthesize such lactam based polyacetylenes? I think that lactams have the ability to complex valuable compounds. PVP is very valuable as a water soluble polymer that can form complexes with iodine, acidic medicinals, and is nontoxic. Just look at how it is promoted by its manufacturers. The schemes 1-4 are “PVP” variations that should be in some cases water soluble but as polyacetylenes they would be conductive and have electronic applications. They would also be colored and

be easily detected in-vivo if targeted with a complexed medicinals.

Thank you for reading this proposal. Please feel free to contact me with any suggestion or corrections.

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