Potential "Vinyl" Lactam Monomers?

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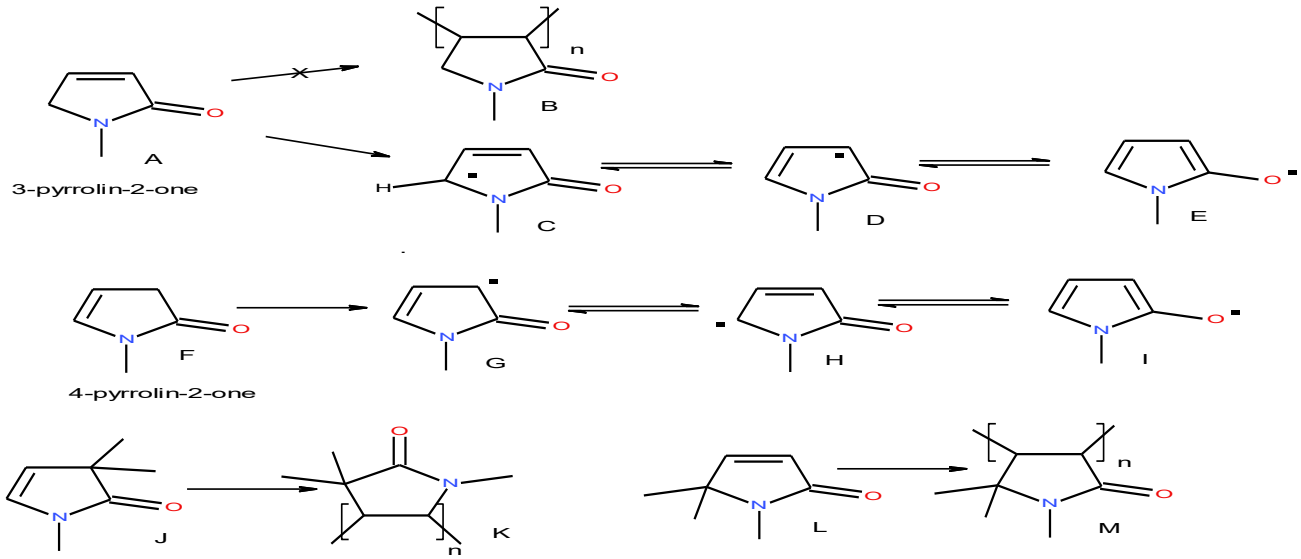
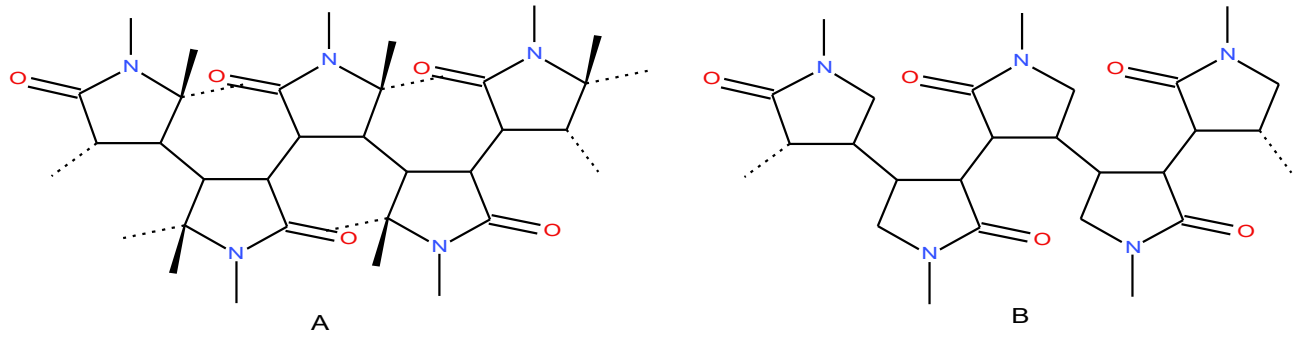
I found myself thinking about structures related somehow to n-vinylpyrrolidone and whether or not they would polymerize by a free radical mechanism? I think that the reason that the following structures don't polymerize by a free radical mechanism, is probably well known but was not obvious to me.



Scheme 1: I've searched and searched and have not found B, K or M in the literature. I think that C-E & G-I are the reasons? Especially E&I where aromaticity is possible. So can J&L polymerize because aromaticity is blocked? The dimethyl groups could be in the way sterically?

https://pubchem.ncbi.nlm.nih.gov/compound/444570

https://pubchem.ncbi.nlm.nih.gov/compound/1_5_5-Trimethylpyrrol-2-one#section=2D-Structure

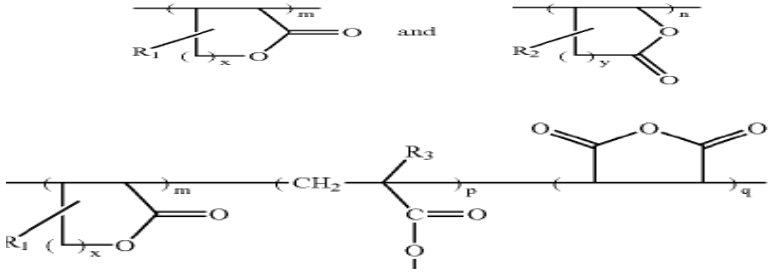


Scheme 2: It looks like the methyls might be a problem with both K&M? Although this simple diagram of this polymer might show steric hindrance, it does not show that the pyrrolidones could be connected in cis or trans relationships that would reduce steric effects. B above would be OK if that monomer would polymerize but I can't find any

evidence for it?

Pelkey, E. T., Pelkey, S. J., & Greger, J. G. (2019). Reactions of 3-pyrrolin-2-ones. In *Advances in Heterocyclic Chemistry* (Vol. 128, pp. 433-565). Academic Press.

Cyclic monomers according to the excellent “Principles of Polymerization” by G. Odian are not good monomers because they are related to 1,2-disubstituted ethylenes(page 277 4th ed.). He indicates that steric hindrance is a big factor and that's why cyclic monomers like maleic anhydride will polymerize because the cyclic structure reduces steric effects. . Other types of cyclic potential monomers are not discussed, however. Therefore, albeit there are steric issues, cyclic monomers do polymerize.



(R_3=methyl, R_4=2-methyl-adamantyl)

12.0 g 2-methyladamantylmethacrylate (MAdMA), 3.4 g maleic anhydride (MA), and 1.66 g α-angelicalactone (AGL) were dissolved in 17 g tetrahydrofuran (THF). 1.38 g dimethyl 2,2'-azobisisobutyrate (V601) was added to the solution, degassed and polymerized at 70° C. for 20 hours.

After the reaction was completed, the obtained reaction product was precipitated with excess isopropyl alcohol twice, filtered, and dried in a vacuum oven for 24 hours, so that the terpolymer having the formula above was obtained with a yield of 72%.

The obtained terpolymer had a weight average molecular weight (Mw) of 11,400, and a polydispersity (Mw/Mn) of 2.4.

In the synthesis of the terpolymer, the mixing ratio of the monomers can be varied to adjust the solubility of the polymer. The various mixing ratios of the monomers and the characteristics of the resultant five terpolymers are listed below in Table 1.

TABLE 1

Mixing Ratio of Monomers (MAdMa:MA: AGL)	Con-centration of Initiator (mol %)	Solvent-to-Monomer ratio (by weight)	Polymeriza-tion Time (hr)	Yield (%)	Mw	Mw/Mn
3:4:1	AIBN 0.05	0.5	24	68	32,100	3.3
3:3:1	AIBN 0.05	0.5	24	87	21,000	2.2
3:2:1	AIBN 0.05	0.5	24	80	17,300	2.7
3:1:2	V601 0.05	1	20	56	7,200	1.7
3:2:1	V601 0.05	1	20	73	9,800	2.8

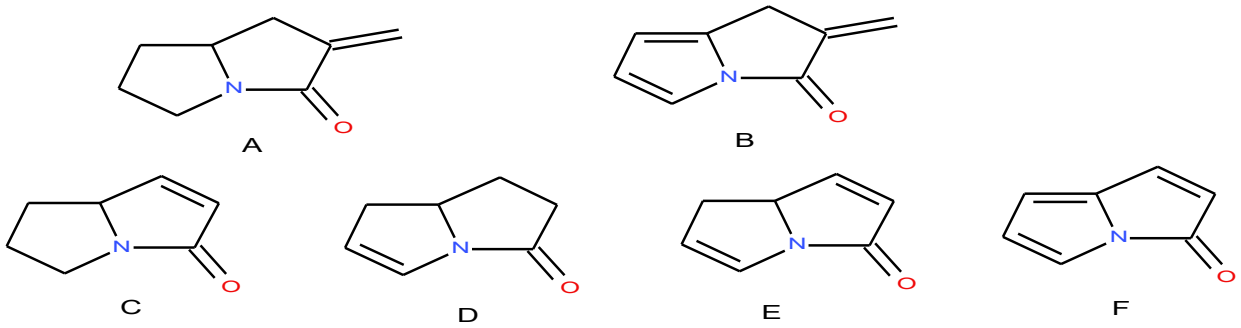
(12) **United States Patent**
Yoon et al.

(10) **Patent No.: US 7,045,267 B2**
(45) **Date of Patent: *May 16, 2006**

Also:

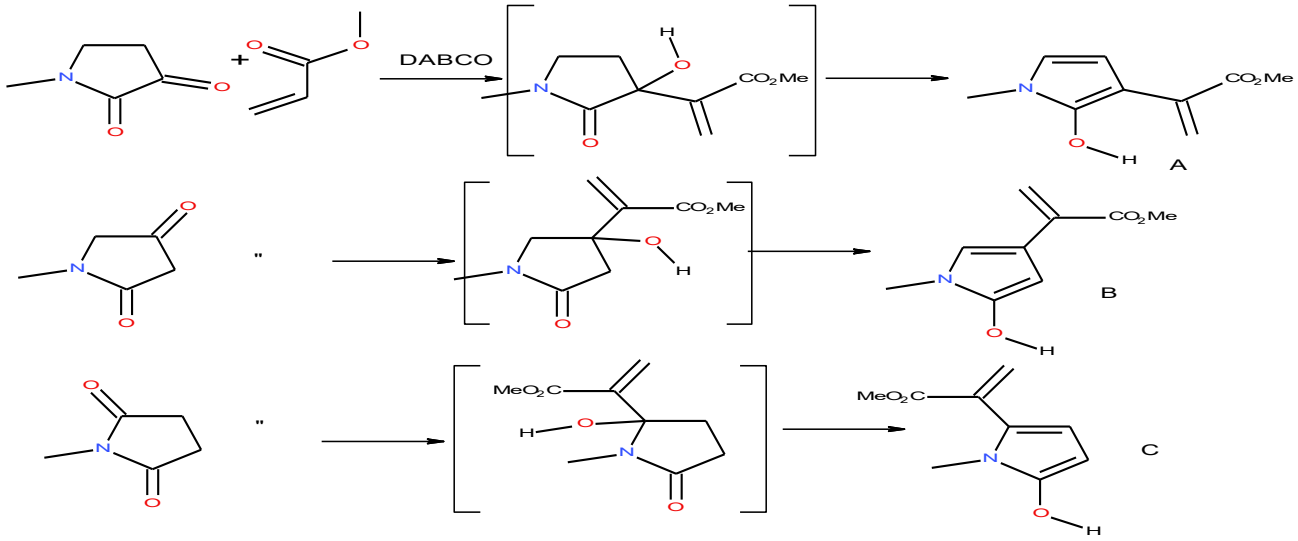
Kaygorodov, K. L., Tarabanko, V. E., & Tarabanko, N. (2018). Thermodynamics of α-angelicalactone polymerization.*Cogent Chemistry*, *4*(1), 1443689.

This suggests that co- or tertiary monomer mixtures based polymers are more easily polymerized.

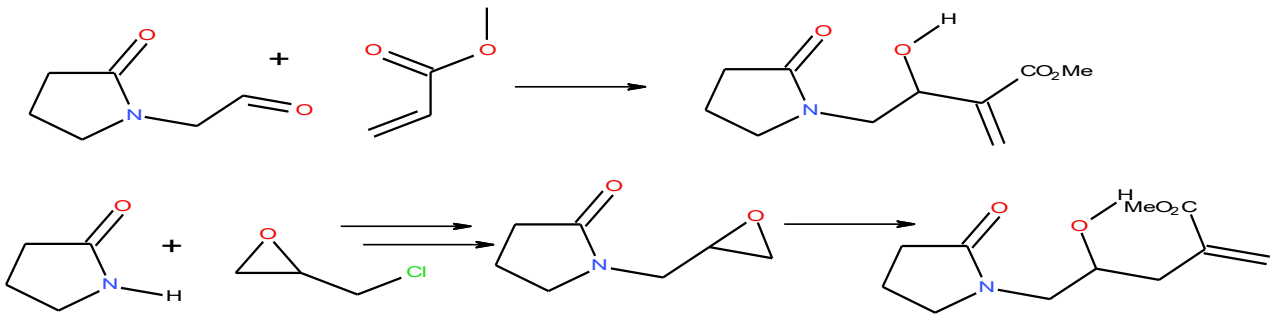


Scheme 3: I would expect A&B to polymerize(see my web page for pdf's of similar structures), however, do C-F polymerize? I'm suggesting that C is a cyclic acrylamide, D cyclic vinyl pyrrolidone, E is a combination of C&D and F an aromatic version. I'm using the pyrrolizine(pyrrolam) bycyclics as examples but other sized rings can also be considered.

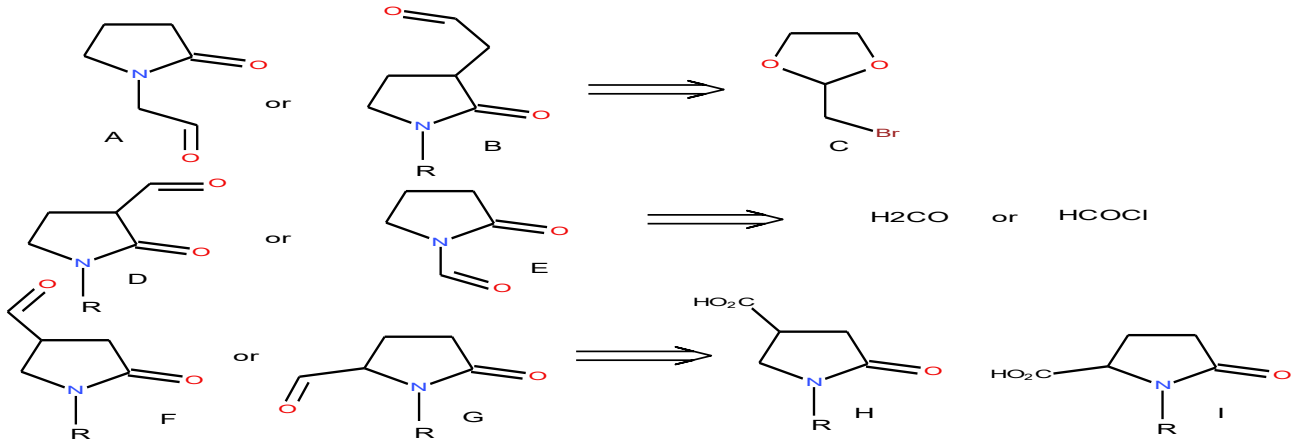
Watson, R. T., Gore, V. K., Chandupatla, K. R., Dieter, R. K., & Snyder, J. P. (2004). Synthesis of (−)-(R)-Pyrrolam A and Studies on Its Stability: A Caveat on Computational Methods. *The Journal of organic chemistry*, *69*(18), 6105-6114.



Scheme 4: MBH(Morita,Baylis, Hillman) reaction with oxopyrrolidones. Polymerization would be through the acrylic portion of these compounds; however, in the pyrrol form because of aromatic stability, A-C would react with a free radical initiator like AiBN for example and polymerize while the pyrrol should not be affected.



Scheme 5: Additional MBH type reactions. I'm betting that the hydroxyl groups survive and do not result in unsaturation conjugated with the acrylic double bond as that might be a problem?

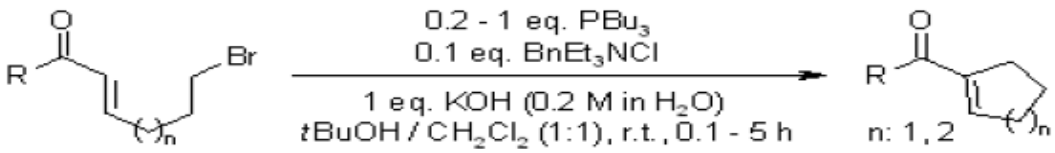


Scheme 6: Potential precursor aldehyde groups can be visualized at every position. I've already discussed these MBH ideas in a prior pdf (rloginconsulting.com) but not in this detail.

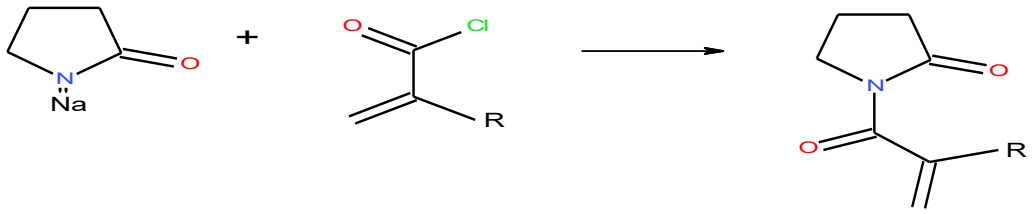
Peng, C., & Joy, A. (2014). Baylis–Hillman Reaction as a Versatile Platform for the Synthesis of Diverse Functionalized Polymers by Chain and Step Polymerization. *Macromolecules*, *47*(4), 1258-1268.

Man, S. K., Wang, X., Zheng, J. W., & An, Z. S. (2020). Effect of Butyl α-Hydroxymethyl Acrylate Monomer Structure on the Morphology Produced via Aqueous Emulsion Polymerization-induced Self-assembly. *Chinese Journal of Polymer Science*, *38*(1), 9-16.

Zhang, Y., Shen, Z., Yang, D., Feng, C., Hu, J., Lu, G., & Huang, X. (2010). Convenient Synthesis of P t BA-g-PMA Well-Defined Graft Copolymer with Tunable Grafting Density. *Macromolecules*, *43*(1), 117-125.

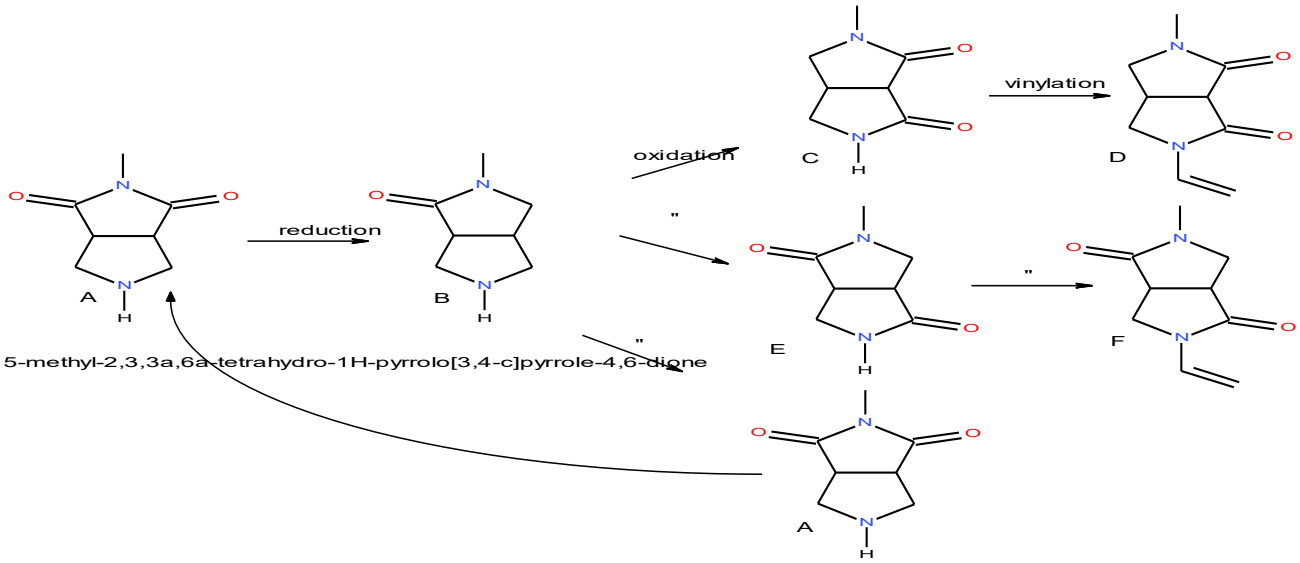


Organocatalysis of the Morita-Baylis-Hillman Alkylation Using Trialkylphosphines
M. E. Krafft, K. A. Seibert, *Synlett*, **2006**, 3334-3336.



1-prop-2-enoylpyrrolidin-2-one

Scheme 7: A pyrrolidone amide acrylate. This compound is known and is in the literature(https://pubchem.ncbi.nlm.nih.gov/compound/543203). Even though it should polymerize, it might not be relatable to PVP; however, because the amide and lactam are in conjugation. It is an interesting monomer.

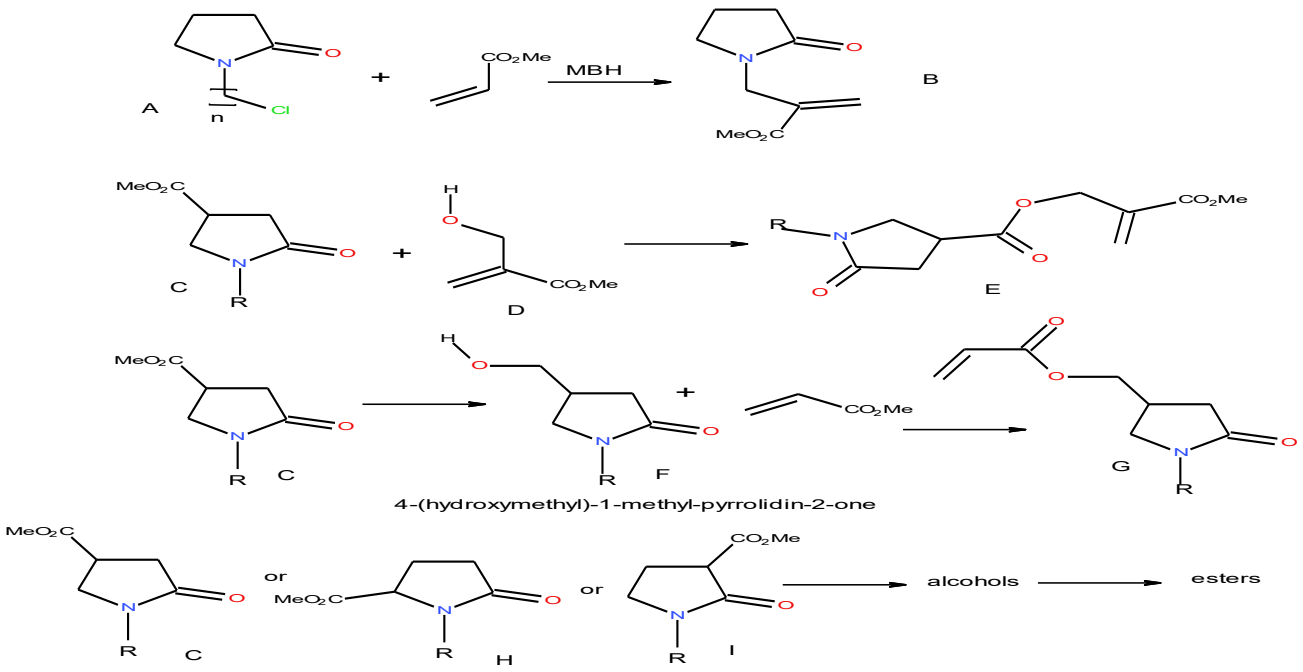


Scheme 8: A is synthesized from maleimide with a [3+2] cycloaddition.

See: Pandey, G., Banerjee, P., & Gadre, S. R. (2006). Construction of enantiopure pyrrolidine ring system via asymmetric [3+ 2]-cycloaddition of azomethine ylides. *Chemical reviews*, *106*(11), 4484-4517.

B through F would require experimentation but the steps would employ well known reactions with readily available reagents.

https://pubchem.ncbi.nlm.nih.gov/compound/75530975
https://pubchem.ncbi.nlm.nih.gov/compound/20761877
https://pubchem.ncbi.nlm.nih.gov/compound/54233419
https://pubchem.ncbi.nlm.nih.gov/compound/118214307

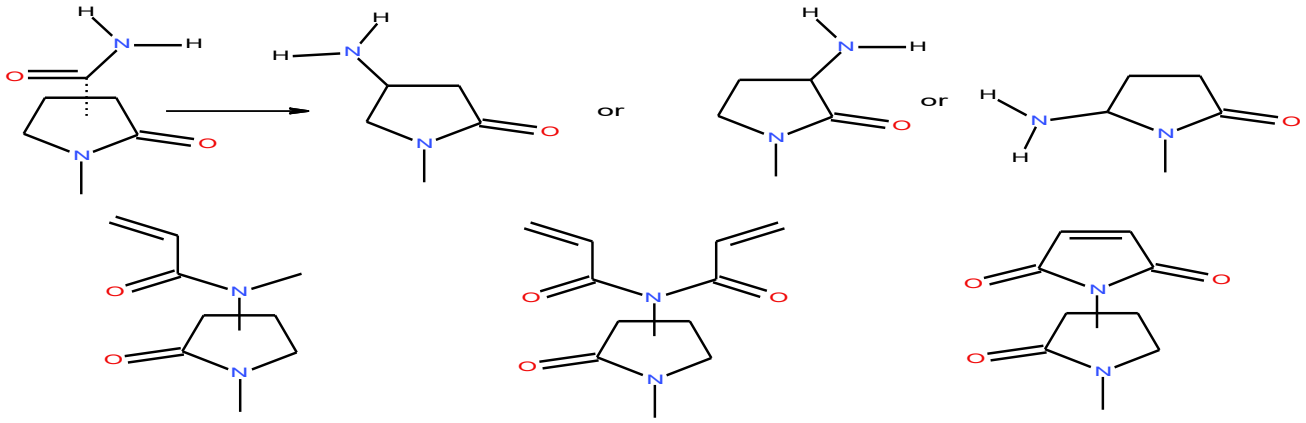


Scheme 9: Additional ideas for polymerizable monomers. Example E and G are examples of building off the itaconic acid starting compound. For additional examples see: US4933463A, US4946967A, US4987210A, US4981974A, US4985521A.

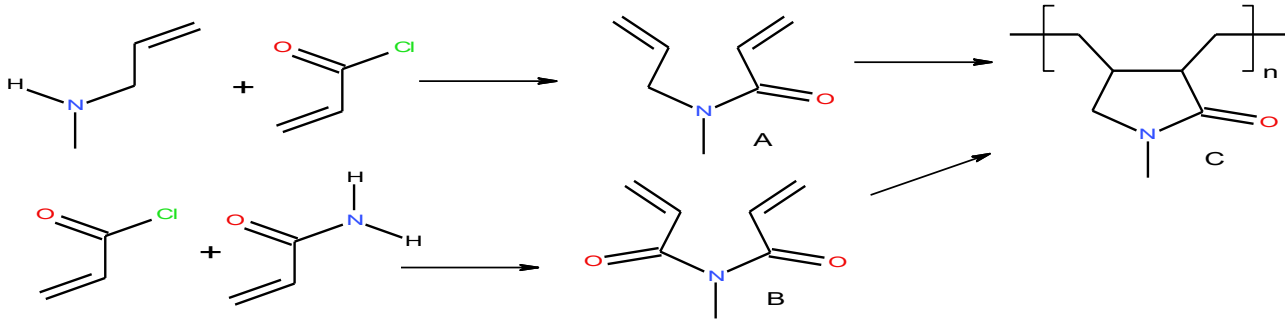
RINGDAHL, B., & CRAIG, J. C. (1980). Circular Dichroism of 3-Hydroxy-2-pyrrolidone. *Acta Chem. Scand. B*, *34*(10).

Angelucci, L., Calvisi, P., Catini, R., Cosentino, U., Cozzolino, R., De Witt, P., ... & Giuliani, A. (1993). Synthesis and amnesia-reversal activity of a series of 7-and 5-membered 3-acylamino lactams. *Journal of medicinal chemistry*, *36*(11), 1511-1519.

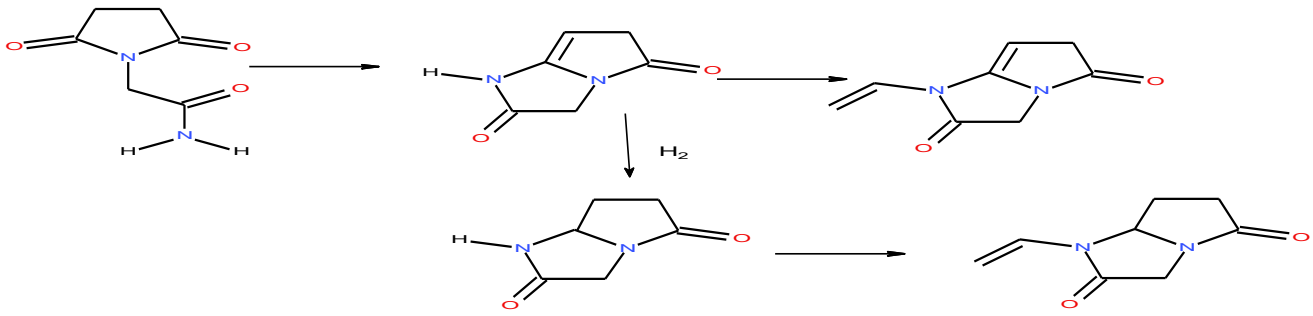
US 2013/0203815 A1
Bandgar et al.
US 201302O3815A1
(43) Pub. Date: Aug. 8, 2013



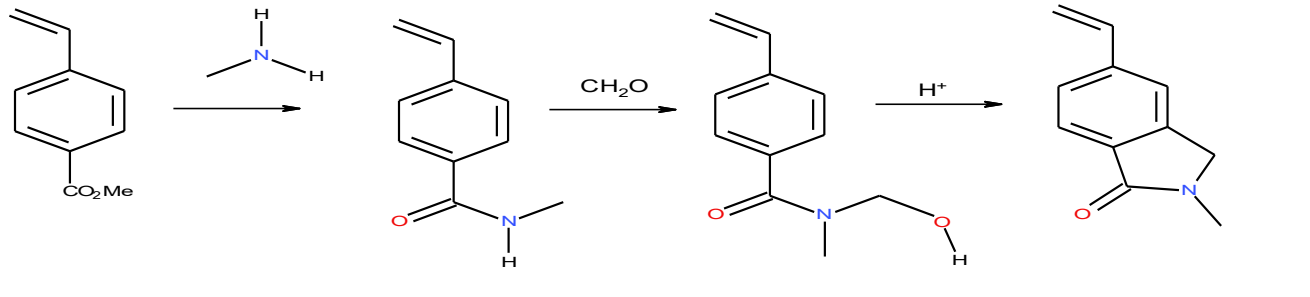
Scheme 10: Several ideas for FR polymerizable amide monomers. Amines can be prepared by the Schmidt Reaction or Curtius Rearrangement, for example.



Scheme 11: Cyclopolymerization possibility. I dont think that A to C works because of the much greater reactivity of the acrylamide part of the compound. Route B to C with a reduction step seems possible.

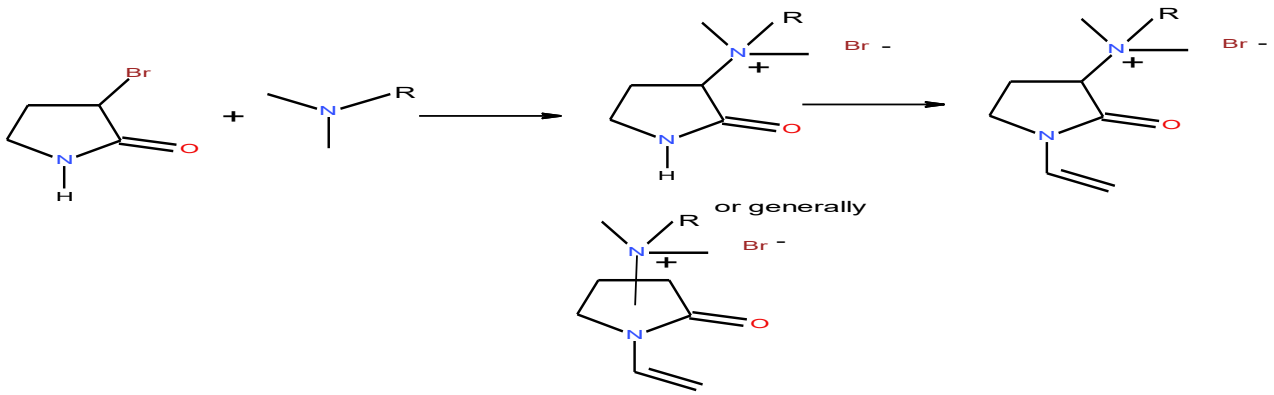


Scheme 12: A dimer type monomer that might be possible.



Scheme 13: Another possibility that seems doable.

Finally, let me suggest a polyquat that if doable would certainly be useful.



Scheme 14: This type of polyquat might have biocidal properties or be useful in cosmetic and hair care applications. Possibly, elimination of the bromide might be a problem? You could then start with the primary amine using formaldehyde to synthesize the tertiary amine then generate the quat.

Thanks for your interest in these proposals!

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