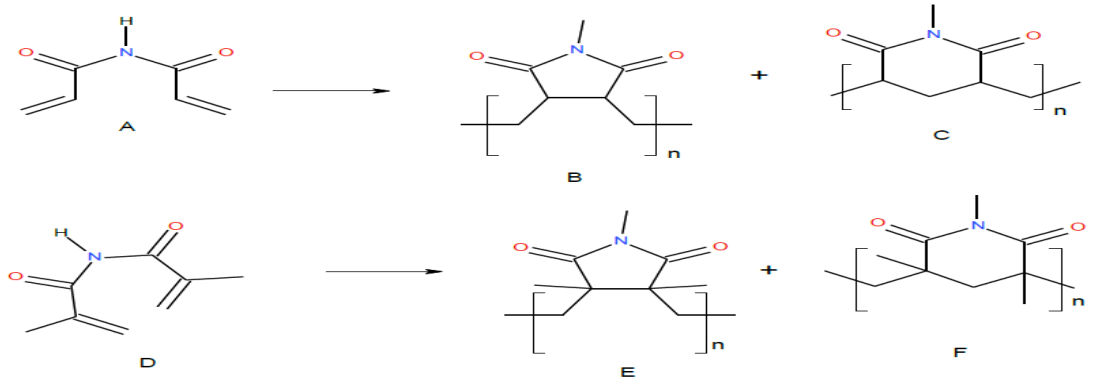
Polypyrrolidones and Cyclopolymerization

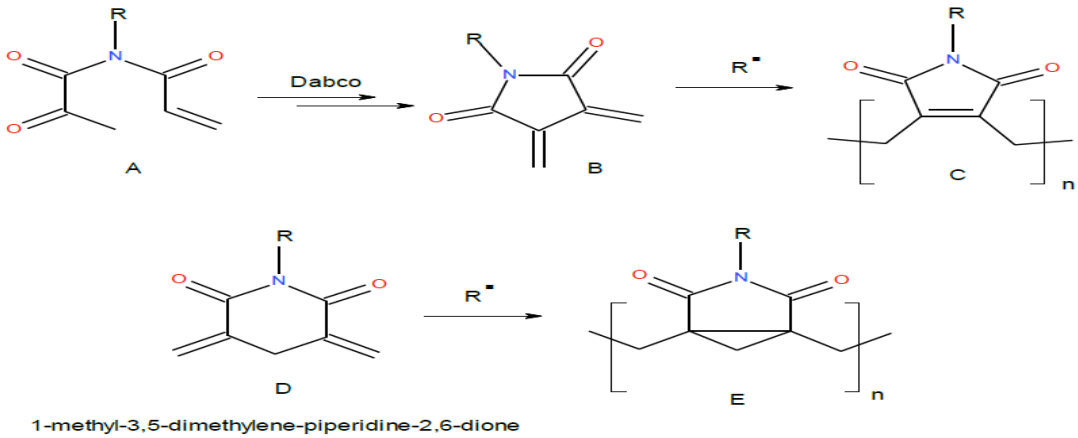
By: Robert B. Login rloginconsulting.com

Vinylpyrrolidone(VP) based polymers are of great importance finding applications in medicinal, pharmacological, cosmetics and other uses. VP can be readily free radical polymerized into homo and copolymers of all types for said applications. After working eleven years for one of the VP manufacturers, I have had a passion for variants of this technology. Look at my web page, you will see that I present numerous pdf's discussing my proposals for new pyrrolidone ideas. What follows is a proposal for employing cyclopolymerization to prepare new pyrrolidone polymers. Lets start with classic cyclopolymerizations.

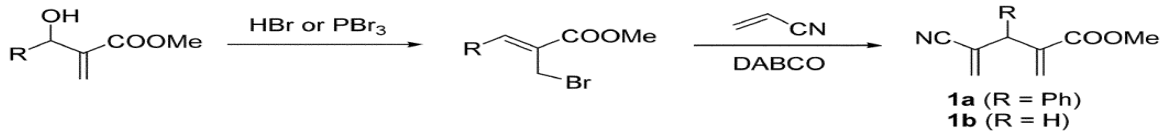


Scheme 1: Cyclopolymerization affords these polymers with the cyclopentane structure in many cases being predominant. This cyclopolymerization was invented by Prof. Butler long ago. Butler, G. (2020). *Cyclopolymerization and cyclocopolymerization*. CRC Press. Reprint of 1992 book (Unfortunately this book is too expensive(~$400) for me to buy but the following review is up to date and worth reading).

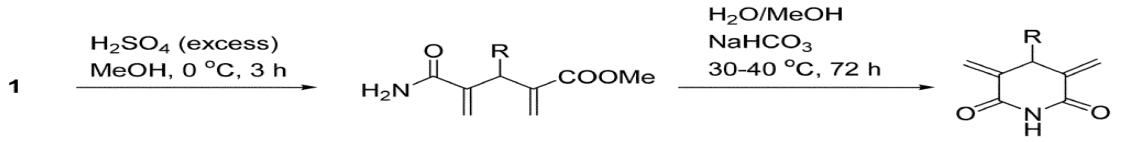
Pasini, D., & Takeuchi, D. (2018). Cyclopolymerizations: Synthetic tools for the precision synthesis of macromolecular architectures. *Chemical reviews*, *118*(18), 8983-9057.



Scheme 2: New imide ideas. The Baylis-Hillman reaction could result in the synthesis of both monomers(D&B).



Scheme 1



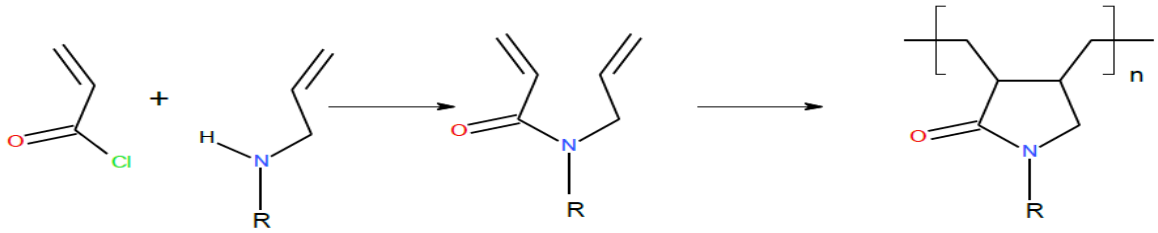
2a (R = Ph), 85%
2b (R = H), 75%

3a (R = Ph), 73%
3b (R = H), 32%

Scheme 2

Lee, M. J., Kim, S. C., & Kim, J. N. (2006). The first synthesis of 3, 5-dimethylene-4-phenylpiperidine-2, 6-dione from Baylis-Hillman adduct. *Bulletin of the Korean Chemical Society*, *27*(1), 140-142.

Although schemes 1&2 are not based on pyrrolidone, it seemed straight forward to do the reactions in scheme 3.



Scheme 3: This seems so straight forward and its in the literature.

Seno, M., Ikezumi, T., Sumie, T., Masuda, Y., & Sato, T. (2000). Asymmetric cyclopolymerization of N-tert-butyl-N-allylacrylamide in the presence of β-cyclodextrin. *Journal of Polymer Science Part A: Polymer Chemistry*, *38*(11), 2098-2105.

Maier, M., Schmidt, M. S., Ringwald, M., & Fik, C. P. (2017). Highly reactive, liquid diacrylamides via synergistic combination of spatially arranged curing moieties. *Beilstein journal of organic chemistry*, *13*(1), 372-383.

Kodaira, T., & Sakaki, S. (1988). Cyclopolymerization, 14. Influence of temperature on free-radical cyclopolymerization of N-allylmethacrylamide and N-allylacrylamide. *Die Makromolekulare Chemie: Macromolecular Chemistry and Physics*, *189*(8), 1835-1844.

The problem is that some allyl derivative may survive the polymerization to some modest extent.

Fukuda, W., Takahashi, A., Takenaka, Y., & Kakiuchi, H. (1988). Cyclopolymerization of N-Alkyl-N-allylacrylamides. *Polymer journal*, *20*(4), 337-344.

The size of the N-R group has a significant effect with larger R groups resulting in more cyclopolymerization. With any surviving allyl containing polymers, crosslinking is

however possible.

Cyclopolymerization. XIX. Effect of *N*-substituents on cyclopolymerizability of *N*-allylmethacrylamides

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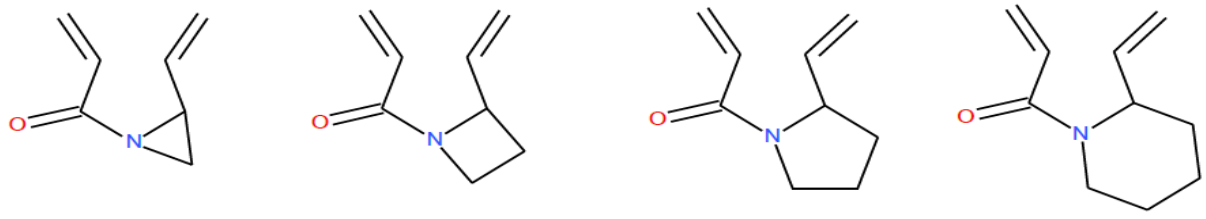
https://doi.org/10.1002/pola.1993.080310120

Abstract

The effect of bulky *N*-substitutents of *N*-*t*-butyl- and *N*-phenyl-*N*-allylmethacrylamides (BAMA and PAMA, respectively) on their cyclopolymerizability was investigated. BAMA yielded an almost completely cyclized polymer while the degree of cyclization of poly (PAMA) was about 95%. The latter value indicates that the effect of phenyl group is comparable with that of methyl group, since *N*-methyl-*N*-allylmethacrylamide was reported to give a polymer with a degree of cyclization of 93%. Structural investigation on telomerization products of BAMA and PAMA permitted the assignment of the repeating cyclic units of these polymers to that of a five-membered ring. This structural characteristic was also supported by the observation of five-membered cyclized radicals on ESR measurements of these monomers. Rotation around amide C(t)N bonds of these monomers and related compounds studied by ^{13}C-NMR was found to be strongly dependent on *N*-substituent. The mechanism of the cyclization was discussed in terms of the structure of the ring formed and rotation around amide C(t)N bonds of these monomers. The reactivity of the methacryloyl and allyl groups involved in these monomers were compared based on the information obtained by structural investigation of polymers and telomerization products and by ESR studies. © 1993 John Wiley & Sons, Inc.



Scheme 4: You could sterically force the best comformation for cyclopolymerization. The cyclic derivative structures can also have R groups attached to enhance the steric effect.

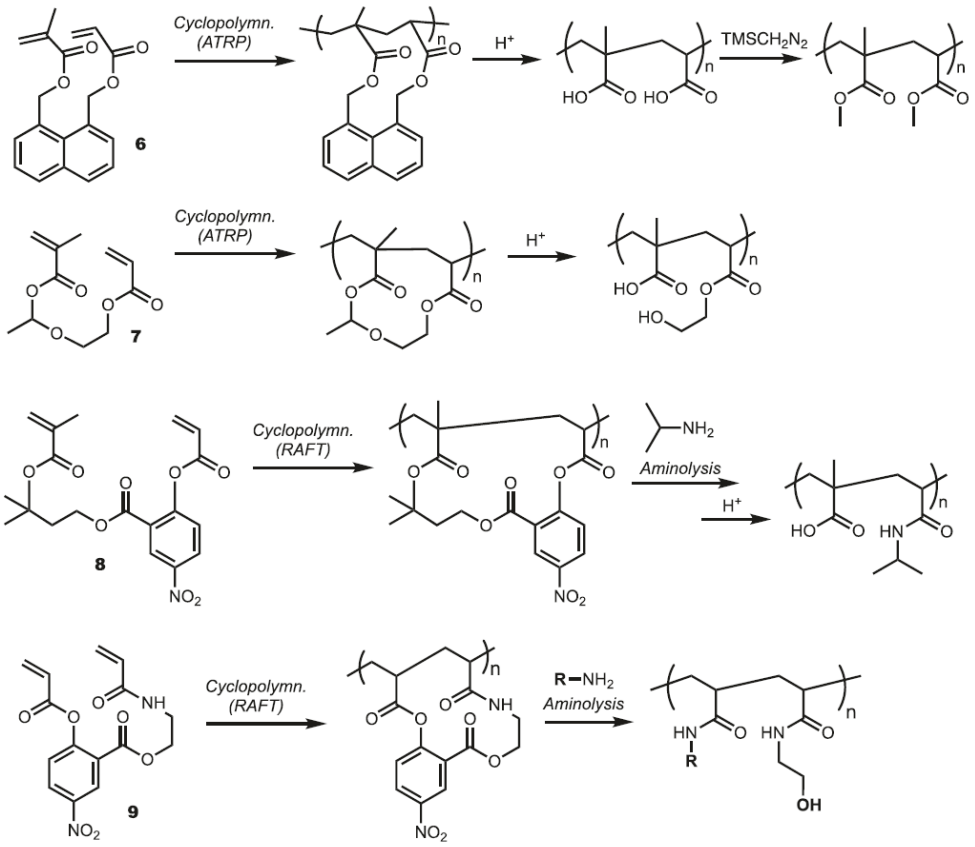
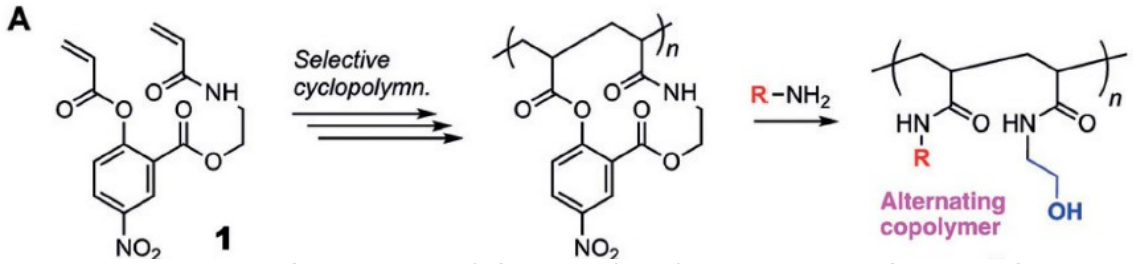


Fig. 6 Examples of divinyl monomers (**6**–**9**) for the synthesis of alternating copolymers via selective cyclopolymerization and subsequent cleavage of the cyclic spacer

Ouchi, M. (2020). Construction methodologies and sequence-oriented properties of sequence-controlled oligomers/polymers generated via radical polymerization. *Polymer Journal*, 1-10.



Kametani, Y., Tournilhac, F., Sawamoto, M., & Ouchi, M. (2020). Unprecedented Sequence Control and Sequence-Driven Properties in a Series of AB-Alternating Copolymers Consisting Solely of Acrylamide Units. *Angewandte Chemie*, *132*(13), 5231-5239.

Ouchi, M., Nakano, M., Nakanishi, T., & Sawamoto, M. (2016). Alternating sequence control for carboxylic acid and hydroxy pendant groups by controlled radical cyclopolymerization of a divinyl monomer carrying a cleavable spacer. *Angewandte Chemie*, *128*(47), 14804-14809.

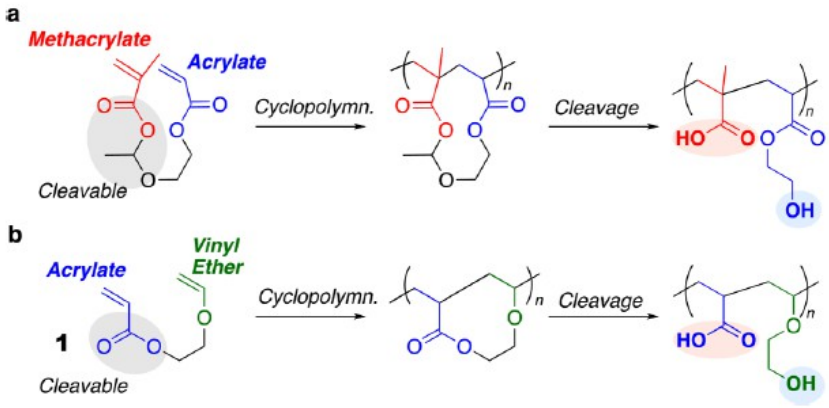
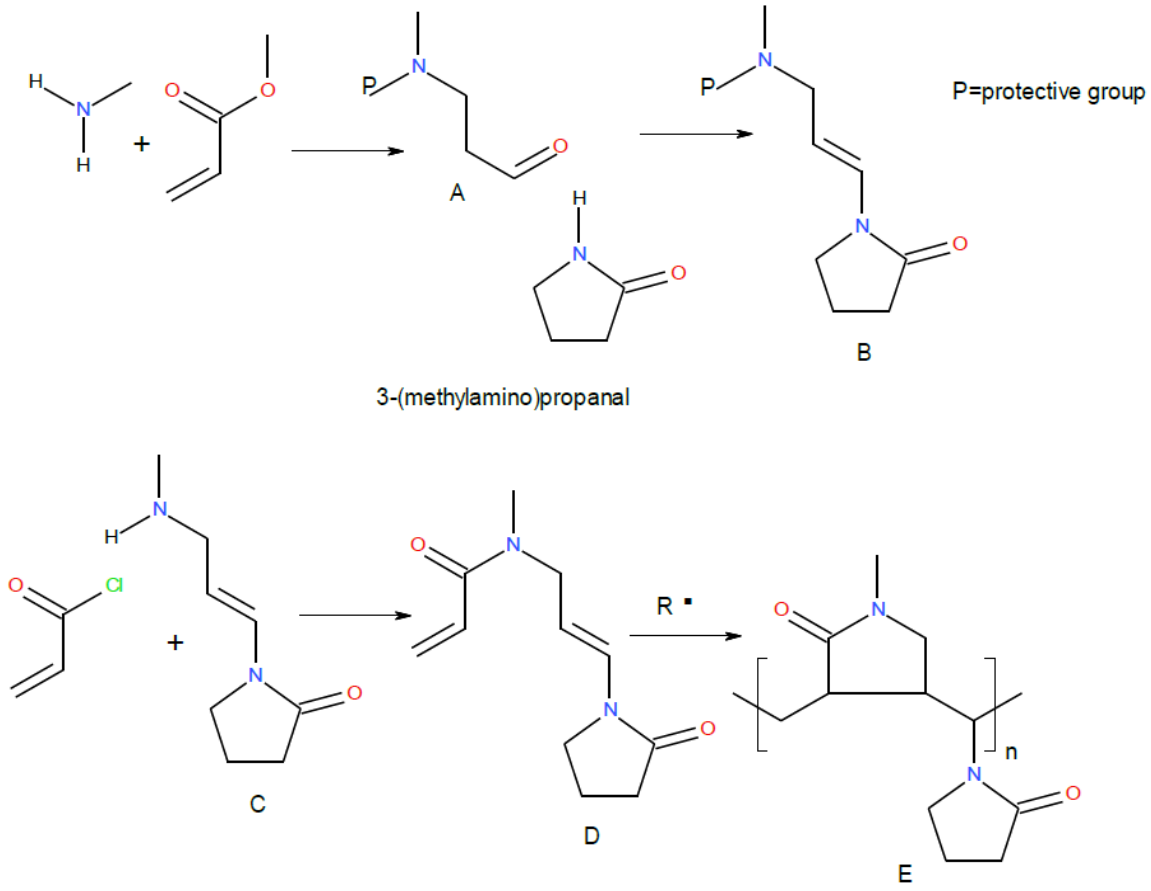


Figure 1. Cyclopolymerizations of cleavable divinyl monomers and the transformation into alternating copolymers via the pendant cleavage: (a) methacrylate-acrylate divinyl monomer connected via hemiacetal ester bond; (b) acrylate-vinyl ether divinyl monomer connected via ester bond.

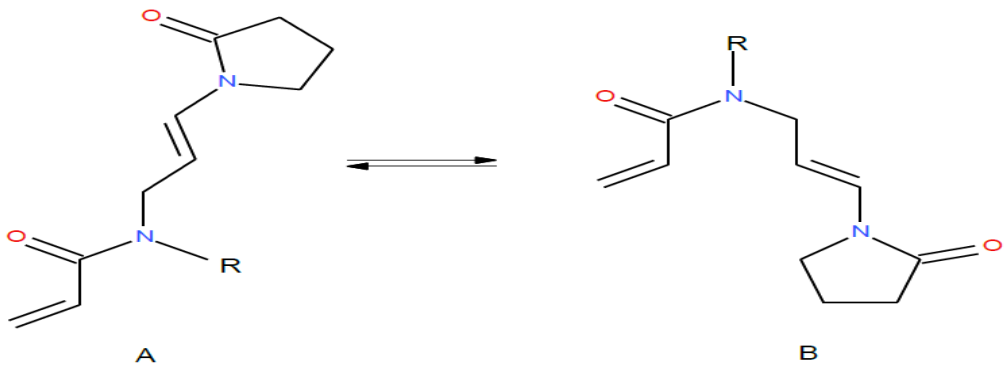
Kametani, Y., Nakano, M., Yamamoto, T., Ouchi, M., & Sawamoto, M. (2017). Cyclopolymerization of cleavable acrylate-vinyl ether divinyl monomer via nitroxide-mediated radical polymerization: copolymer beyond reactivity ratio. *ACS Macro Letters*, *6*(7), 754-757.

The above reviews led me to think of related ideas.

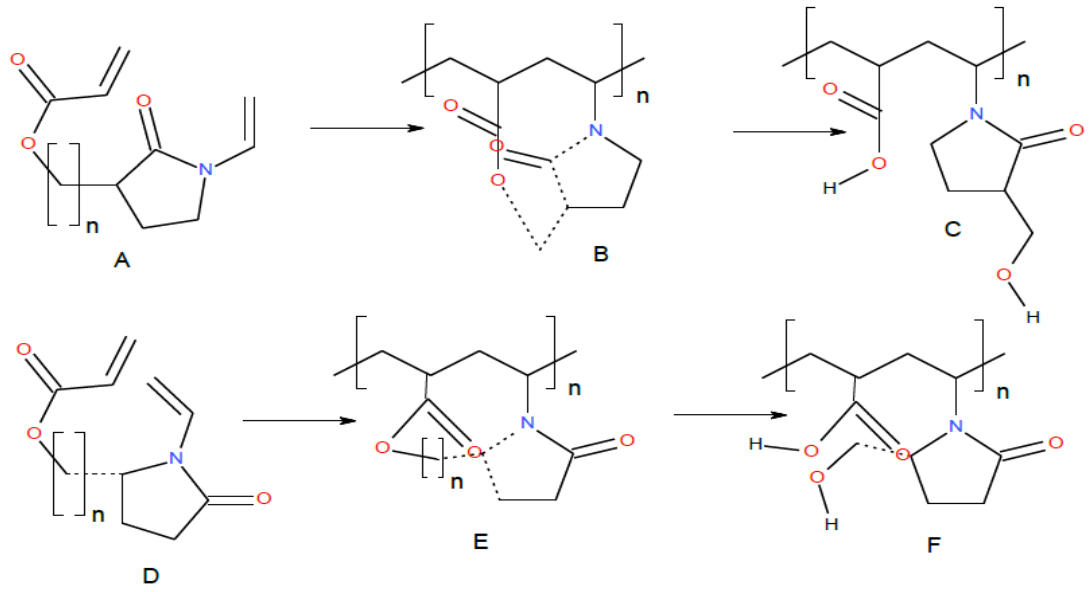


Scheme 5: A way to get both "NMP and PVP" on the same polymer. "NMP" is regarded as a super solvent, while PVP exhibits outstanding complexing ability for large anions. Would E above exhibit both properties?

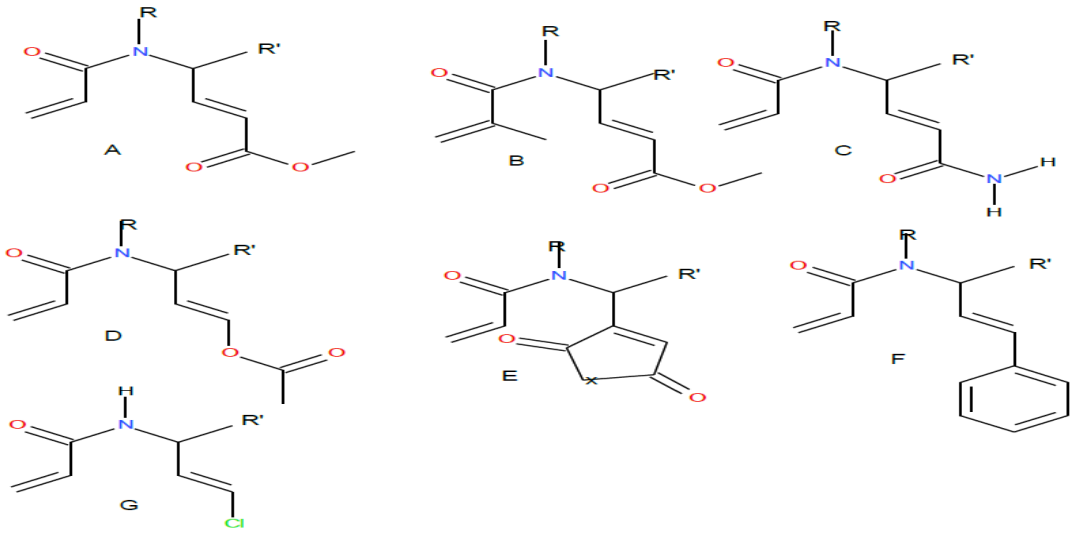
Note that the substituent on the acylamide nitrogen can have an effect on the course of this reaction.



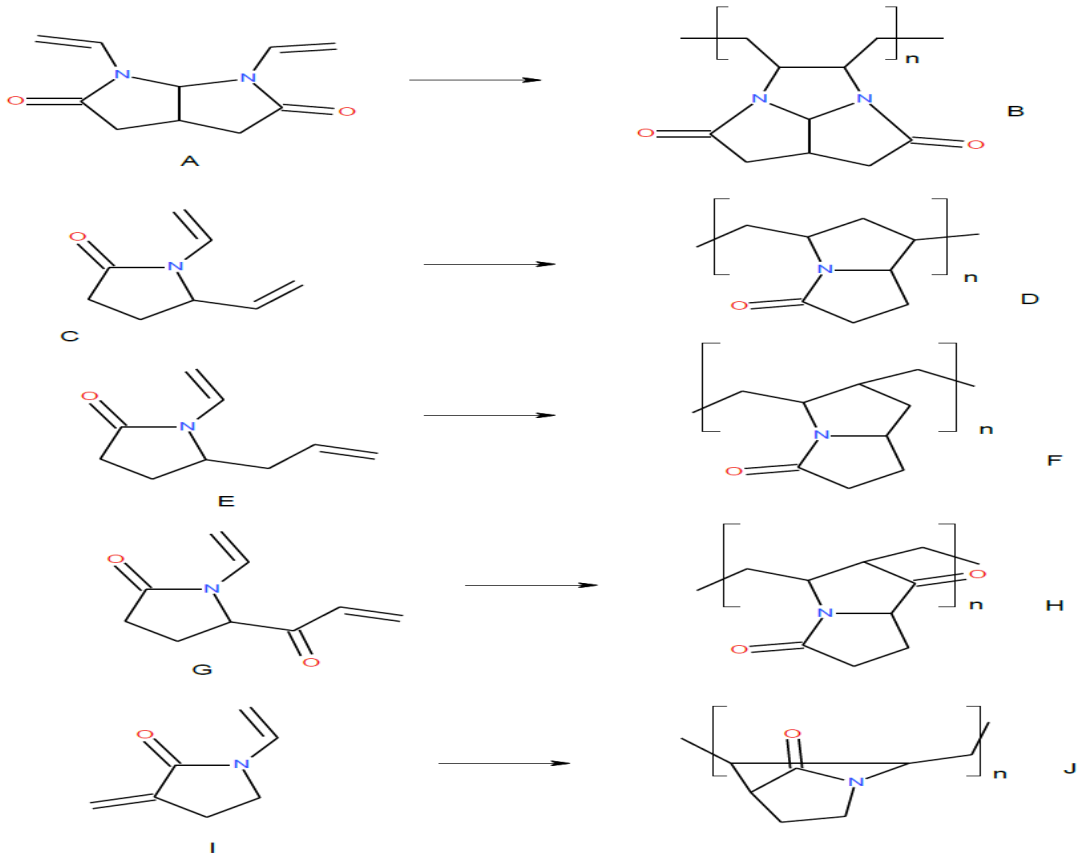
Scheme 6: "A" would result in crosslinking while "B" would afford the desired polymer. From the literature it is known that large R groups and that more dilute concentrations also plays a part in generating the desired polymer.



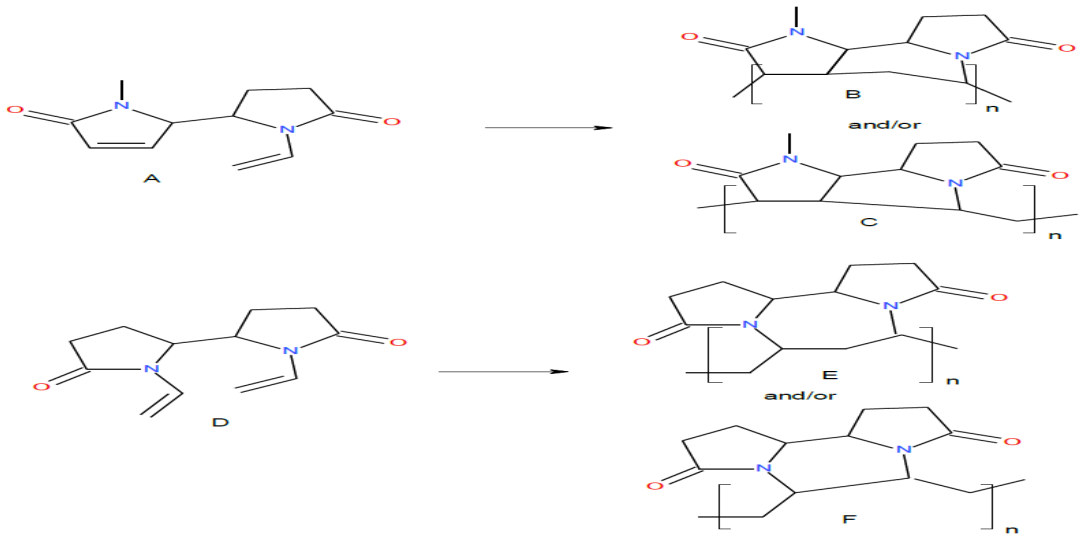
Scheme 7: A&D are examples of using a more active vinyl polymerizable vinyl pyrrolidone monomer. Although an acrylate comonomer is shown other comonomers such as methacrylic or acrylamides and so forth could be employed. Note n=1 with A & D above for clarity.



Scheme 8: Other ideas in this vein employing structures besides VP that could undergo cyclic polymerization.



Scheme 9: More possibilities. Note 5 membered rings are shown but larger rings are also possibilities.



Scheme 10: “Dimer” ideas. I think B & E are more doable but thats my opinion. The advantage of binding these monomers together is the the stereo chemistry is set. This maybe important in their complexing ability with medicinals, for example.

Thank you for reading these proposals.

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