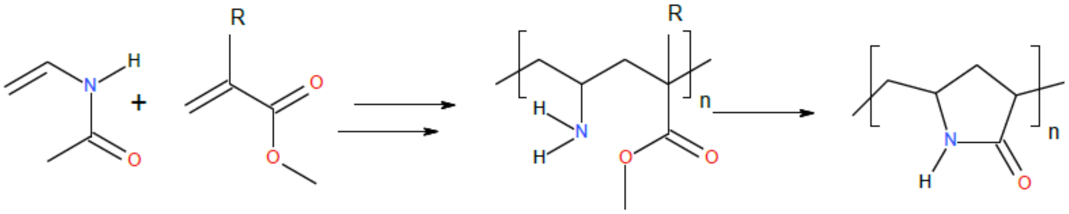
Lactam Chain Polymers

By: Robert B. Login rloginconsulting.com

While researching another idea, I came across the following chemistry:



Scheme 1: Pyrrolidone chain polymers.

The first hurdle would be the necessity of the starting monomers forming alternating copolymers.

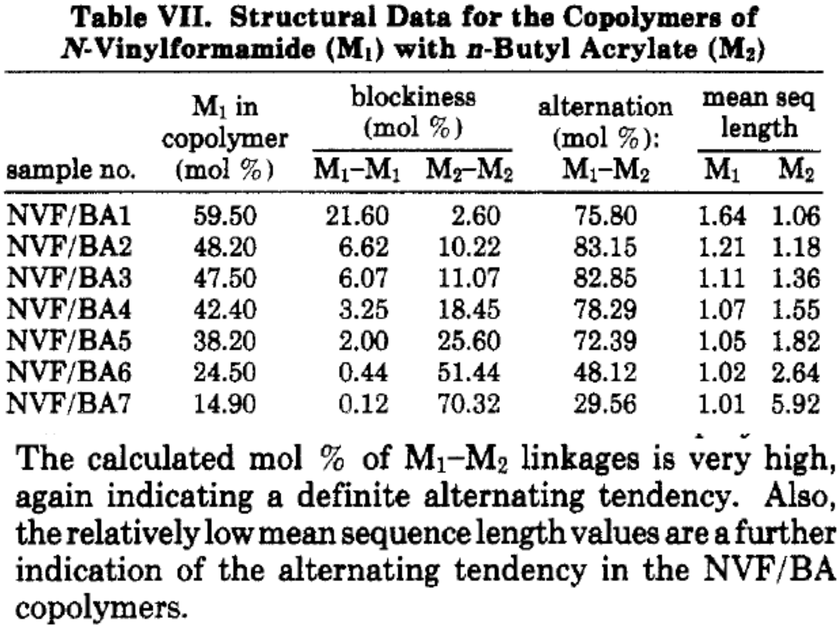
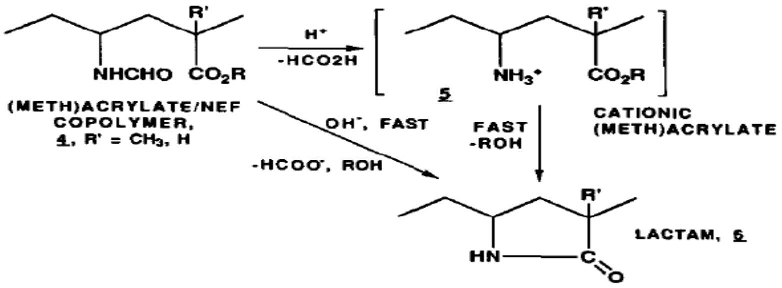


Table VII. Structural Data for the Copolymers of *N*-Vinylformamide (M_1) with *n*-Butyl Acrylate (M_2)

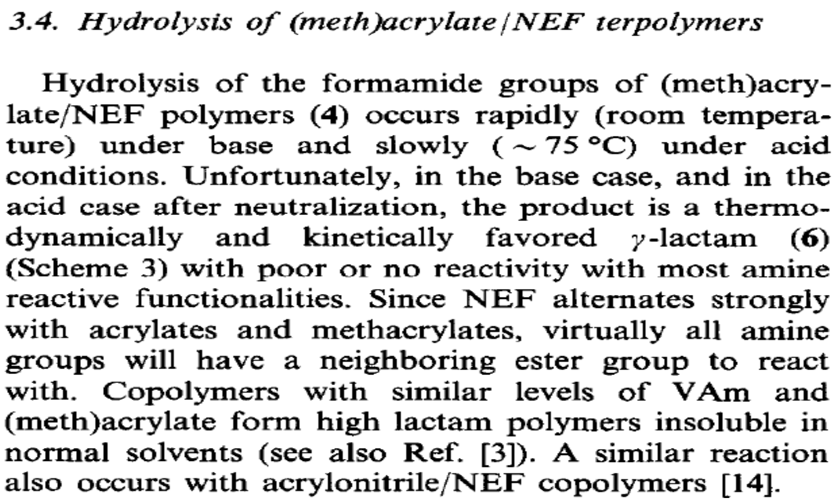
sample no.	M_1 in copolymer (mol %)	blockiness (mol %)		alternation (mol %):	mean seq length	
		M_1–M_1	M_2–M_2	M_1–M_2	M_1	M_2
NVF/BA1	59.50	21.60	2.60	75.80	1.64	1.06
NVF/BA2	48.20	6.62	10.22	83.15	1.21	1.18
NVF/BA3	47.50	6.07	11.07	82.85	1.11	1.36
NVF/BA4	42.40	3.25	18.45	78.29	1.07	1.55
NVF/BA5	38.20	2.00	25.60	72.39	1.05	1.82
NVF/BA6	24.50	0.44	51.44	48.12	1.02	2.64
NVF/BA7	14.90	0.12	70.32	29.56	1.01	5.92

The calculated mol % of M_1–M_2 linkages is very high, again indicating a definite alternating tendency. Also, the relatively low mean sequence length values are a further indication of the alternating tendency in the NVF/BA copolymers.

Kathmann, E. E., & McCormick, C. L. (1993). Water-soluble copolymers. 48. Reactivity ratios of N-vinylformamide with acrylamide, sodium acrylate, and n-butyl acrylate. *Macromolecules*, *26*(19), 5249-5252.



Scheme 3. Lactam formation in (meth)acrylate/NEF copolymers.



3.4. *Hydrolysis of (meth)acrylate/NEF terpolymers*

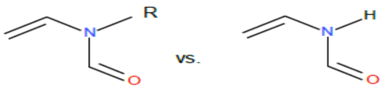
Hydrolysis of the formamide groups of (meth)acrylate/NEF polymers (**4**) occurs rapidly (room temperature) under base and slowly (~75 °C) under acid conditions. Unfortunately, in the base case, and in the acid case after neutralization, the product is a thermodynamically and kinetically favored γ-lactam (**6**) (Scheme 3) with poor or no reactivity with most amine reactive functionalities. Since NEF alternates strongly with acrylates and methacrylates, virtually all amine groups will have a neighboring ester group to react with. Copolymers with similar levels of VAm and (meth)acrylate form high lactam polymers insoluble in normal solvents (see also Ref. [3]). A similar reaction also occurs with acrylonitrile/NEF copolymers [14].

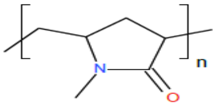
Pinschmidt Jr, R. K., Wasowski, L. A., Orphanides, G. G., & Yacoub, K. (1996). Amine functional polymers based on N-ethenylformamide. *Progress in organic coatings*, *27*(1-4), 209-218.

Pinschmidt Jr, R. K. (2010). Polyvinylamine at last. *Journal of Polymer Science Part A: Polymer Chemistry*, *48*(11), 2257-2283.

Several patents also deal with this chemistry.
Patent Number: 5,281,340 and 5,512,645

I would have thought that although of great interest to me, there would be many references citing this chemistry? But I have found none. Why do I think that having pyrrolidones in the polymer backbone is interesting? I already covered this in a previous pdf (see http://rloginconsulting.com/joomla/images/SiteFiles/Patents/pyrrolidone%20backbone%20polymers.pdf) When I wrote this pdf, I was unaware of the above references. So what else do I think this chemistry might contribute?

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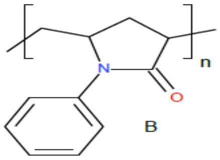
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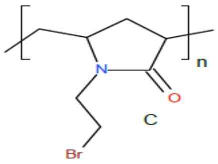
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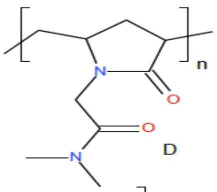
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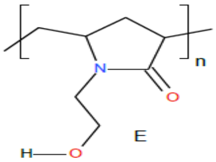
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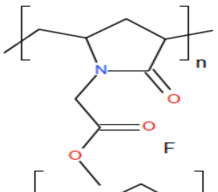
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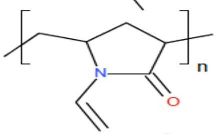
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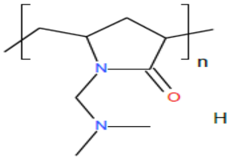
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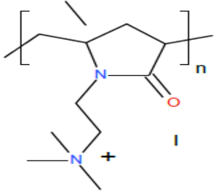
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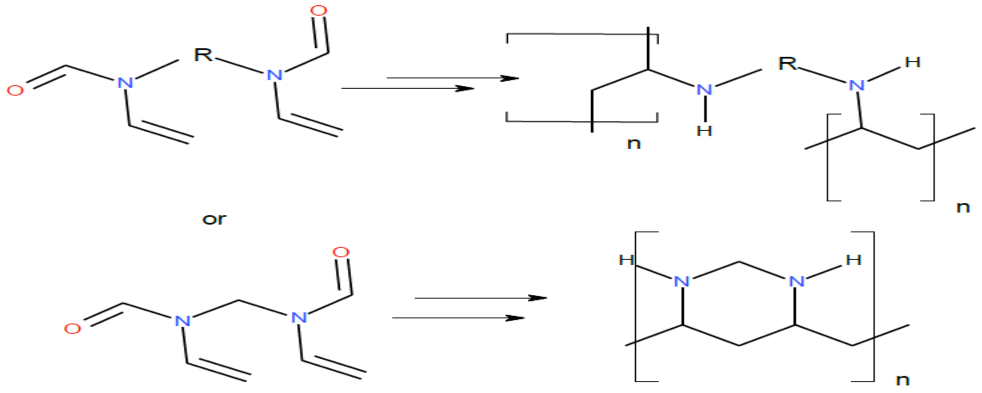
Scheme 2: New potential structures and many more could be suggested. The question is if an R group on nitrogen would prevent or inhibit the pyrrolidone formation? G would be partially vinylated after pyrrolidone formation. In fact some derivative reactions of the pyrrolidone amide nitrogen could also be conducted to one extent or another after polymerization.

Also how difficult might hydrolysis be to the free substituted amine that is required to react with the ester? See:

Dréan, M., Guégan, P., Jérôme, C., Rieger, J., & Debuigne, A. (2016). Far beyond primary poly (vinylamine) s through free radical copolymerization and amide hydrolysis. *Polymer Chemistry*, *7*(1), 69-78.

Synthesis of monomers see:

White, L. A., Hoyle, C. E., Jönsson, S., & Mathias, L. J. (2005). Effects of cis–trans isomerization on the photopolymerization behavior of N-vinyl amide monomers. *Designed monomers and polymers*, *8*(4), 297-308.



Scheme 3: Although not related to the synthesis of pyrrolidones, this idea crossed my mind. Synthesis from aldehydes and N-ethenylformamide should be possible.

Thank you for your interest!

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