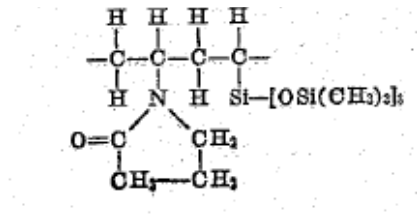


Silicone-Pyrrolidone Copolymers

By: Robert B. Login

Silicones (siloxanes) have been successful as cosmetic ingredients; however, as I understand it, they are not as popular as in the past? (<http://www.besthealthmag.ca/best-looks/beauty/the-truth-about-silicones/>). One of the problems is the claim that they block skin pores and cause acne because of their very non-polar nature which makes them hard to remove with soap and water. To counter some of the problems with silicones, I suggest combining them with pyrrolidone functionality. This is not to say that this concept cannot be approached with other water soluble groups. The patent literature contains many such examples (especially look at the patents to Siltech); however, I have not found references for the following ideas.

Pyrrolidone exhibits unique properties such as water solubility, film formation, very low toxicity, compatibility to mention a few. This is not a new idea as I have found patents describing this chemistry. The earliest patent USP 2,820,798 shows how to use vinyl siloxanes to prepare copolymers with NVP.



vinyl siloxane. Such copolymers are particularly useful in view of their water solubility which makes them especially valuable as emulsifying agents in dimethylpolysiloxane oil-water systems. Our copolymers are also soluble in aliphatic ketones such as acetone. In addition the copolymers of our invention can also be employed as additives for lubricants, detergents and mold release compounds.

USP 3,832,458 for example:

The present invention provides a composition comprising a copolymer of a silicone elastomer and N-vinyl pyrrolidone which has limited but significant permeability toward water soluble materials and the degree of permeability can be regulated by controlling the amount of N-vinyl pyrrolidone and the method of forming the layer through which permeation is derived.

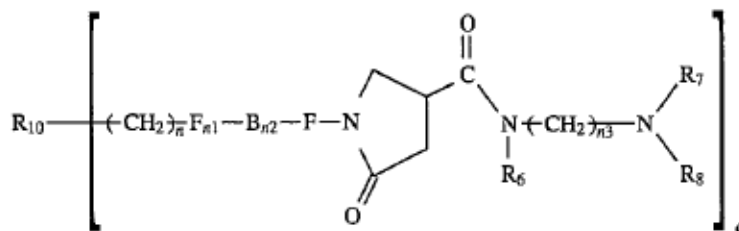
USP 4,055,682:

[57]

ABSTRACT

A silicone catheter is rendered hydrophilic by contacting it with N-vinyl pyrrolidone (NVP) in bulk or in solution and exposing the catheter and NVP to ionizing radiation at high dose rate. Penetration of the NVP beyond a thin surface layer is prevented by controlling the dose of ionizing radiation and the concentration of NVP.

USP 5,596,061:



or its
pound

30 wherein:

R₁₀ is a silicone backbone chain as herein described to which at least one pyrrolidone containing carboxyl functional group or amidoamine derivative thereof is attached as hereinabove shown;

The polysiloxane compositions according to the present invention are useful, for example, for reducing the friction of petroleum flow through pipelines as well as being precursors for a wide range of personal care products, fiber treating agents and the like which impart such advantages as improved feel, substantivity, reduced surface tension, and anti-stick characteristics.

USP 8,053,513:

(57)

ABSTRACT

The properties of 2-pyrrolidone-4-carboxylic substituted polysiloxanes can be dramatically altered by increasing the presence of the carboxylic-substituted pyrrolidone monomer of the polysiloxane, such that the amidopolysiloxane has an acid equivalent weight of about 3:00-3,000 daltons and a molecular weight average Mw of about 1,000-60,000 daltons resulting in enhanced detergent and water solubilities and the ability to form water-in-oil emulsions thereby providing usefulness across a broad range of formulations having enhanced electrolytic and silicone and/or hydrocarbon compatibility and cleansing properties.

Others are USP 4,138,382, USP 4,172,101, and 5,274,028. My goal here is not to do a exhaustive literature search as I would expect many other examples could be found. I would rather put forward my own ideas for useful copolymers.

Hydrosilylation:

Macromolecules, Vol. 32, No. 9, 1999

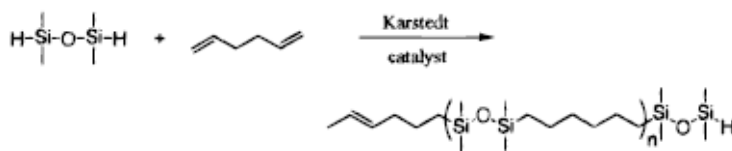
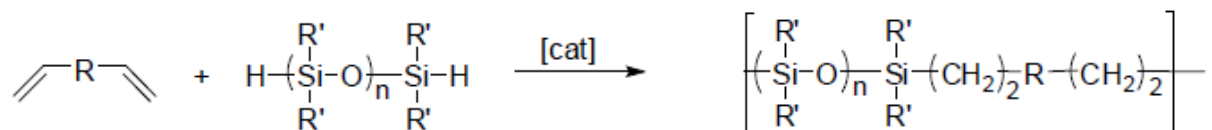


Figure 1. Hydrosilylation copolymerization 1,5-hexadiene and 1,3-dihydroditetramethylsiloxane.

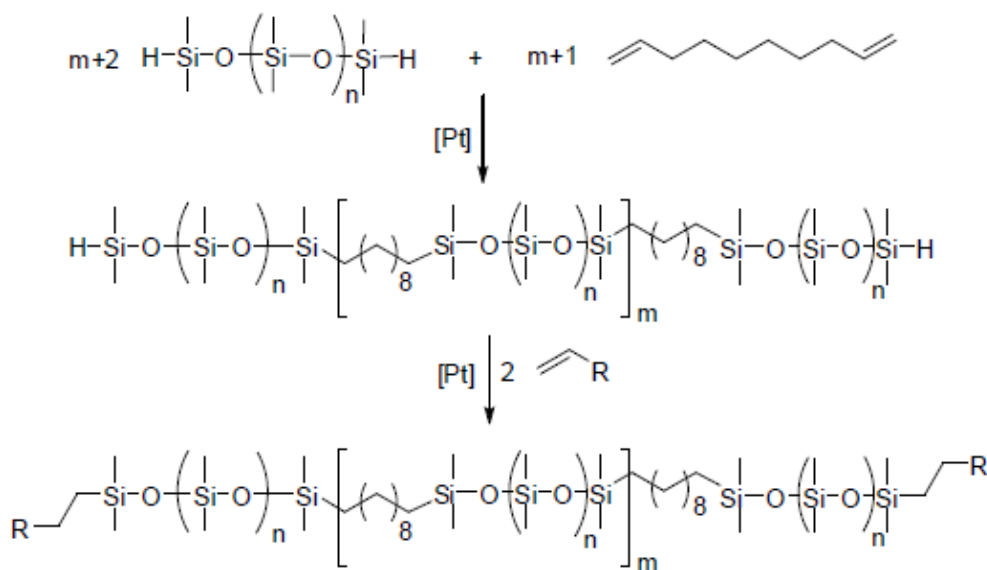
The above example illustrates how hydrosilylation can be employed to generate copolymers. Only a dihydrosiloxane is shown however the technology for placing the hydrosilylation group at the ends of much bigger silicones is well established.

(poly)hydrosilylation route:



Scheme 1.2. Synthesis of polysilalkylene siloxanes (hybrid silicones) via condensation and hydrosilylation.

By adjusting the stoichiometry, a wide variety of siloxanes with hydrosiloxane end groups can be obtained. For example:



R = CH₂-Si(OMe)₃, CH₂-NH₂, CH₂-glycidyl, ...

Scheme 1.3. Synthesis and functionalization of a polysilalkylene siloxane.

The above examples are from the dissertation of S. Putzien, “Functionalized Hybrid Silicones- Catalysis, Synthesis and Application” 2012. This thesis contains a wealth of information concerning this topic(<https://mediatum.ub.tum.de/doc/1097001/1097001.pdf>).

It is also possible to incorporate Si-H groups within the polymer chain. Even high levels can be incorporated thus leaving open the ability to use hydrosilylation to functionalize these siloxane copolymers with pyrrolidone groups(see J.L. Gormly et. al., US 8,053,513 2011). The well known reaction of amines with itaconates is employed in this patent.

TABLE 1

Ex	Aminopolysiloxane X	M_w^*	M_n^*	Amidopolysiloxane X	R^2	a:b	Acid Eq Wt
1	—NH ₂	20,000	7,500		Me	66:1	4400
2	—NH ₂	40,000	20,000		Me	25.4:1	2250
3	—NH ₂	50,000	30,000		Me w/40%	25.6:1	2300
4	—NH ₂	3000	910		EtO	4.5:1	450
5	—NH ₂	10000	3400		Me	29.4:1	2410

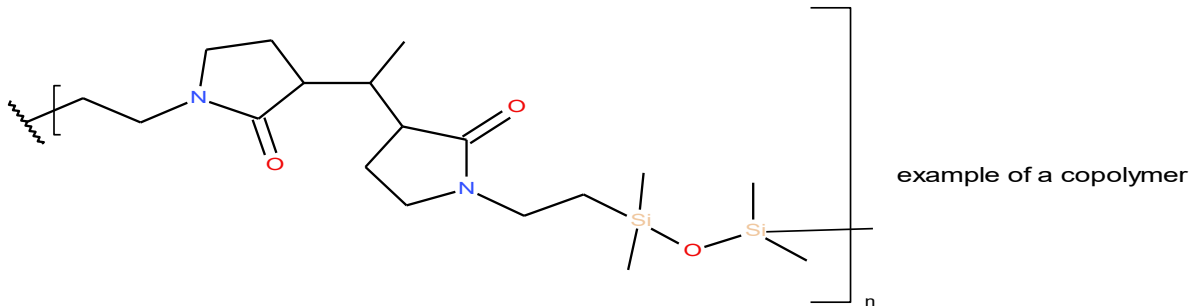
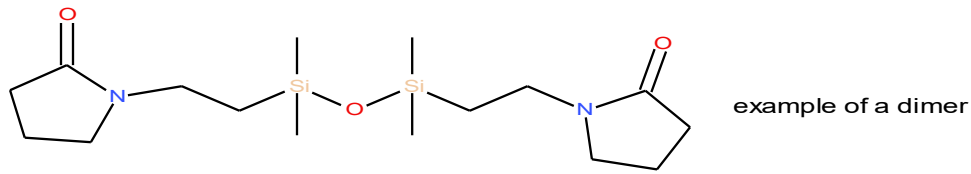
* M_w and M_n of the aminopolysiloxane starting material.

Said polymers are claimed to have a variety of uses including

ing in enhanced detergent and water solubilities and the ability to form water-in-oil emulsions thereby providing usefulness across a broad range of formulations having enhanced electrolytic and silicone and/or hydrocarbon compatibility and cleansing properties.

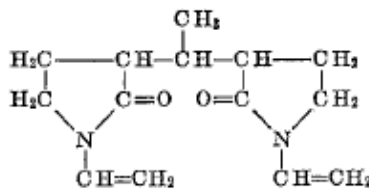
Another example is the 2012 patent by O'Lenick et. al. US 8,263,061 B2 which illustrates the same type of idea but this time with cationic pendant groups.

Obviously NVP could be substituted to synthesize other derivatives with a siloxane backbone and with pyrrolidone pendant groups. For example:

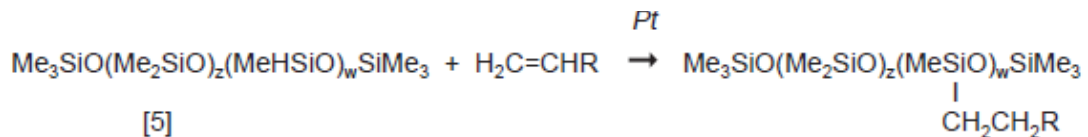


The “N,N'-Divinyldipyrrolidone” is readily available according to Hort et. al., US 3,252,995, 1966.

The pure product has the following structure:



The other approach to pyrrolidone containing siloxanes is by the following route:

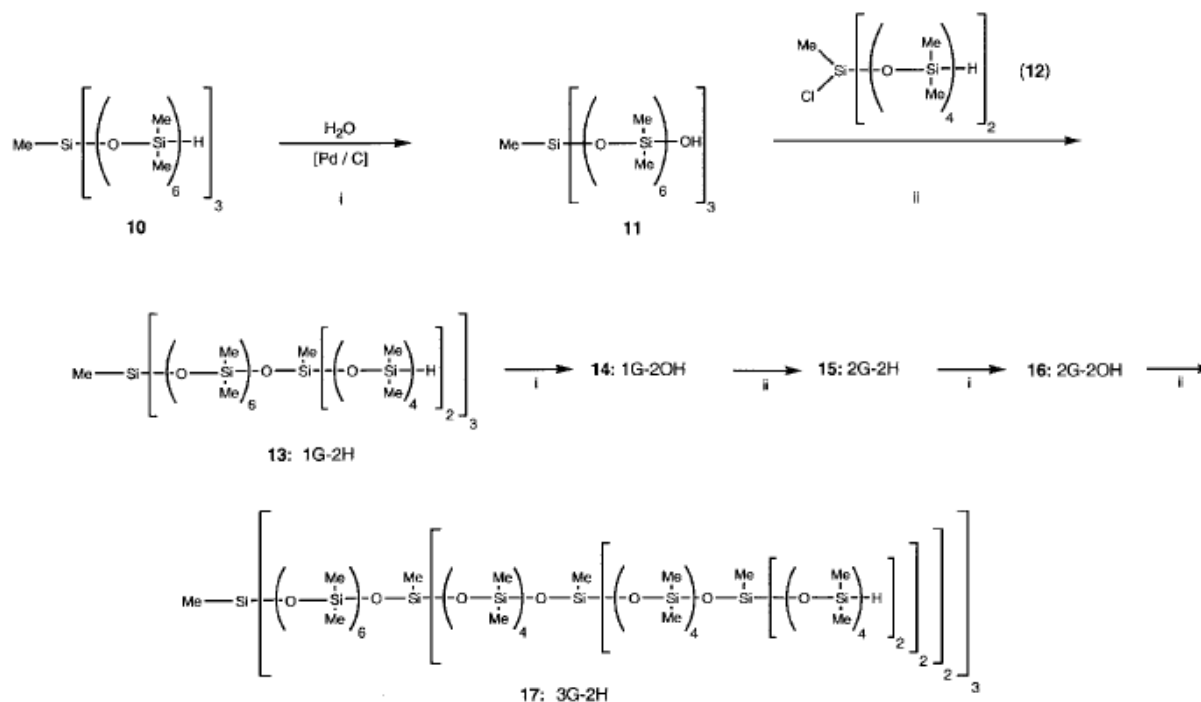


In this case R=pyrrolidone. I would think that as the percentage of pyrrolidone increases that water solubility would increase or a variety of gels would result. Upon dry-down, I would expect that as the pyrrolidone level increases, the neat polymer would go from a liquid, to a paste, to a film. Since these hydrosiloxanes can be generated with left over reactive groups that could also be condensed with acrylic tertiary amines such as

DMAEMA etc.. Such copolymers would be cosmetic candidates for hair conditioning or components for skin care products. The possible advantage of pyrrolidone copolymers would be easy removal because of aqueous solubility or sensitivity (no pore blocking), film forming on hair and skin retaining the desired silicone feel and low toxicity. Biodegradability is supposedly not a problem with silicones.

I would also point out the utility of dimethoxymethylsilane by itself reacted with NVP as an alternative to preparing a plethora of silicone-pyrrolidone polymers(*Journal of Applied Polymer Science*, Vol. 114, 892–900 (2009)).

Adv. Mater. 2001, 13, No. 20, October 16 is a review of siloxane dendrimers by H. Lang, B. Lühmann. Here is another potential application of pyrrolidone derivatised dendrimers. For example:



Scheme 2. Preparation of the third generation polysiloxane dendrimer **17** (i: catalytic oxidation, ii: alcoholysis) [38].

H. Uchida, Y. Kabe, K. Yoshino, A. Kawamata, I. Isumuraya, S. Masamune, *J. Am. Chem. Soc.* **1990**, *112*, 7077.

At some stage of dendrimer synthesis, the hydrosiloxane can react with NVP affording a

dendrimer coated with pyrrolidones. This type of dendrimer might be a drug delivery candidate, or a source of iodine, or a carrier of biologics such as proteins, RNA, DNA, or of indicators of biological activity. The siloxane groups are not attacked by enzymes or degraded; therefore, they would survive in a biological environment. I can see good and bad about this but these are my suggestions designed to spark interest.

Siloxane chemistry can be very straight forward. The complications arise by the fact that most of the chemistry revolves around equilibration which can be tricky. Because of the huge usage of silicones, the various monomers are available. I think combining pyrrolidone with siloxanes would produce interesting copolymers.

General References:

- M. A. Brook; Silicon in Organometallic and Polymer Chemistry; Wiley, 2000
- R. A. Hill; Silicone Surfactants; Decker, 1999
- J. E. Mark et. al.; The Polysiloxanes; Oxford, 2015
- H. R. Kricheldorf; Silicon in Polymer Synthesis; Springer, 1996

Claims:

1. The reaction of Hydrosiloxanes either terminal or internal with N-Vinyl Pyrrolidone comprising pyrrolidone siloxanes that are more easily removed from surfaces by cleansing said surfaces with soap and water.