

MADIX Polymerization of NVP in the presence of an anionic surfactant
in order to improve PVP tacticity

By: Robert B. Login (rloginconsulting.com)

I can not tell you the current methods of commercial NVP polymerization because I have not worked for someone in that business since 1996; however, I would wager that not much has changed since then? This does not mean that free radical polymerization has not changed. Vast improvements in Controlled Radical Polymerization CRP especially living radical polymerization have occurred. I hardly knew anything about this revolution in 1996 but since then numerous articles and books have appeared concerning this subject. Acronyms such as RAFT, MADIX, NMP, ATRP etc each one stands for a method of CRP with different CTA's (chain transfer agents). The hallmark of these is that the free radical terminal of the growing polymer chain is trapped hence the free radical terminal is in an equilibrium with a trapping agent (CTA). This has the effect that one trapping agent generates one polymer chain. Hence you can control MW and have low polydispersity. You can even add a new monomer after the first one to make block copolymers. All manner of architectures are possible and I direct you to some of the reviews on this subject.

**Handbook of
RAFT Polymerization**

© 2008 WILEY-VCH Verlag GmbH & Co.
KGaA, Weinheim

*Edited by
Christopher Barner-Kowollik*

Macromolecules 2015, 48, 5459–5469

Polymer 49 (2008) 1079-1131

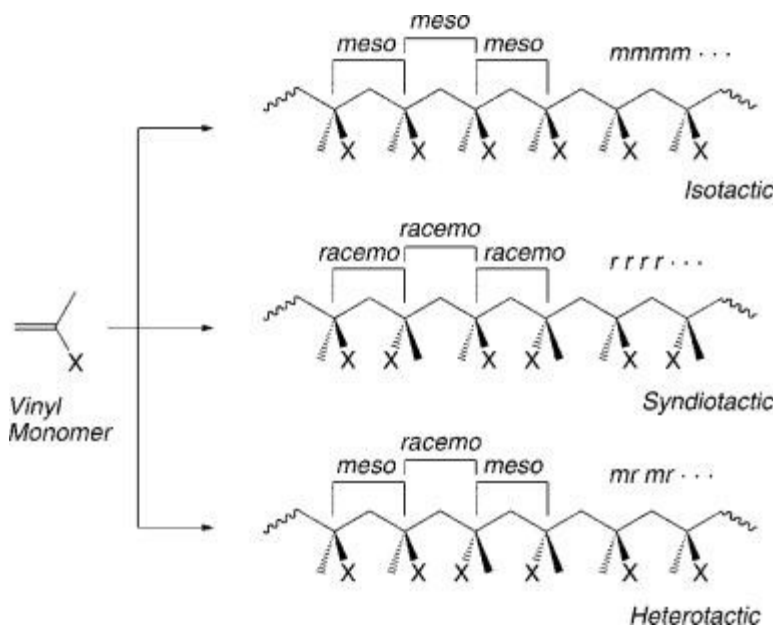
Macromolecules 2012, 45, 5321–5342

Tacticity:

How does tacticity effect PVP?

“The control on stereoregularity affects the polymer properties, like solubility, crystallinity, mechanical properties, melting point, etc.” (Colloid Polym Sci (2015) 293:143–152). It also effects the polymers interaction with surfaces presumably hair and skin in the case of PVP or its copolymers. Because no one has figured out how to control PVP tacticity, its effect on the key uses of PVP wait to be discovered. But one would think it would have a major effect on the ability of PVP to complex with for example iodine or hydrogen peroxide not to mention biological/medicinal agents.

PVP can exist in three tacticities, atactic with all of the pyrrolidone moieties on one side of the polymer chain, syndiotactic with all alternating, or atactic(also called heterotactic) where they are random. Now it is unlikely that currently manufactured PVP would be completely one or the other tacticity and is actually heterotactic.



Polymerization in Fluoroalcohols	monomer solvent or additive temp, °C	triad tacticity			% diad tacticity	
		<i>mm</i>	<i>mr</i>	<i>rr</i>	<i>m</i>	<i>r</i>
NVP bulk	20	31	29	39	46	54
NVP (CF ₃) ₃ COH (SS-5)	-40	19	37	44	37	63

Wan, D.; Satoh, K.; Kamigaito, M.; Okamoto, Y. *Macromolecules* **2005**, *38*, 10397
(m and r above are calculated by $r(\text{or } m) = mr/2 + rr(\text{or } mm)$ by convention.)

The above reference shows that a strong H-bonding solvent and temperature can effect tacticity. This is because of the size of the complex favors syndiotacticity and heat favors heterotacticity (Polym. Chem., 2013, 4, 5449 has a very nice summary)

Another approach is to use a stereo regular template such as PMAA of known tacticities.

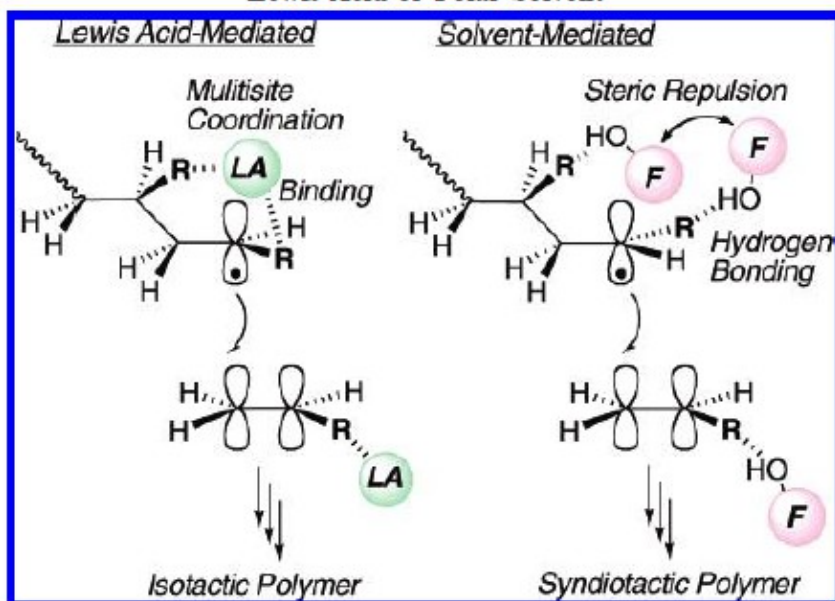
See: Bartels et. al. J. Polym. Sci., J. Polym. Chem. Ed., 1977 and

Y. Y. Tan, Radical Polymerization Along Macromolecular Templates V.215 Nato ASI series pp281-292.....a review 1987.

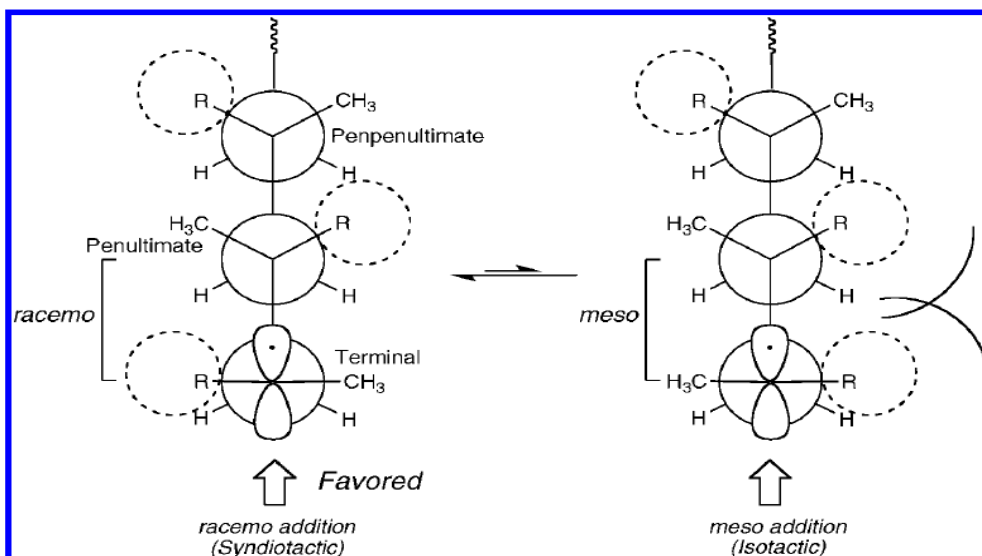
The problem with this technique is how to isolate the resulting PVP from the PMAA. One possibility would be to cross-link the PMAA onto beads or other easily removed surfaces, so that the PVP could be easily recovered.

Macromolecules, Vol. 41, No. 2, 2008

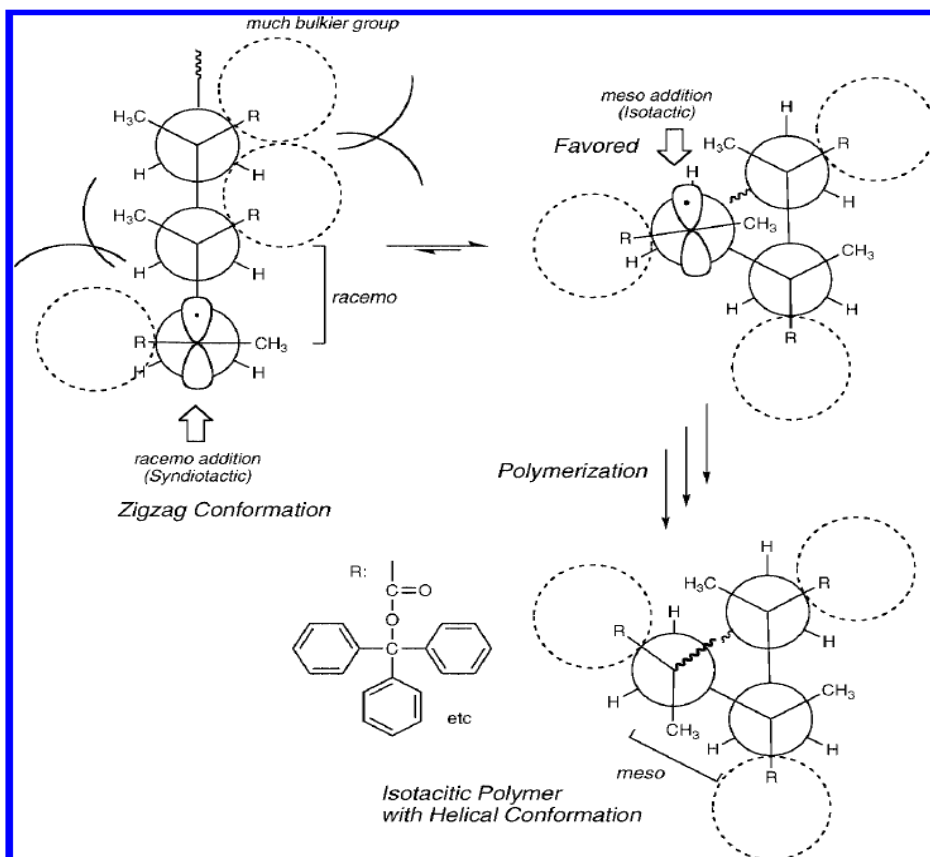
Scheme 2. Stereospecific Radical Polymerizations Mediated by Lewis Acid or Polar Solvent



The above from a review (M. Kamigaito and K. Satoh) shows how solvent and/or additives can interact with the penultimate radical chain end to favor tacticity. Lewis acids that can complex with two adjacent R groups would be expected to result in



12. Schematic models of methacrylate polymerization.

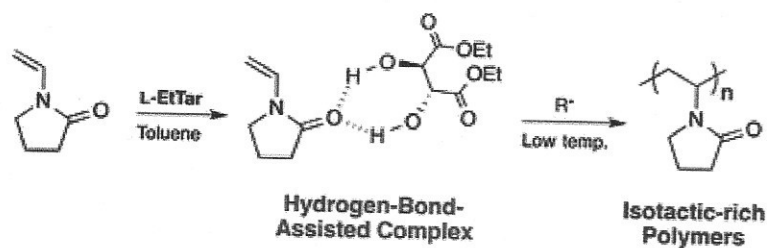


13. Schematic models of bulky methacrylate polymerization.

isotacticity. They show this in the above charts (Chem Rev. 2009, 109, 5120-5156).

Bulky and very bulky groups influences tacticity also shown schematically in the above charts.

A diethyl L-tartrate (L-EtTar)-assisted radical polymerization of *N*-vinyl-2-pyrrolidone has been developed as the first reported example of the synthesis of isotactic-rich poly(*N*-vinyl-2-pyrrolidone) (PVP). The addition of L-EtTar in toluene at temperatures of $-40\text{ }^{\circ}\text{C}$ and lower led to a significant increase in the polymer yield by one order of magnitude compared with the reaction in the absence of L-EtTar. Decreasing the polymerization temperature led to increases in the isotacticity of the PVP, with the *mm* triad reaching 66.4% at $-93\text{ }^{\circ}\text{C}$. ^1H NMR measurement at 920 MHz was conducted to establish a reliable strategy for quantifying the triad tacticities. High-temperature NMR measurements at $250\text{ }^{\circ}\text{C}$ were performed using a specially-designed NMR probe, which led to dramatic narrowing of the ^1H line width.



T. Hirano et. al. RSC Adv., 2014, 4, 53079-53089.

This reference shows that an additive that can H-bond to PVP carbonyl results in an increase in isotacticity. As can be seen from the above figure 13 that large groups results in isotacticity according to the above projections. Another explanation is that the L-EtTar H-bonds to two adjacent pyrrolidone moieties.

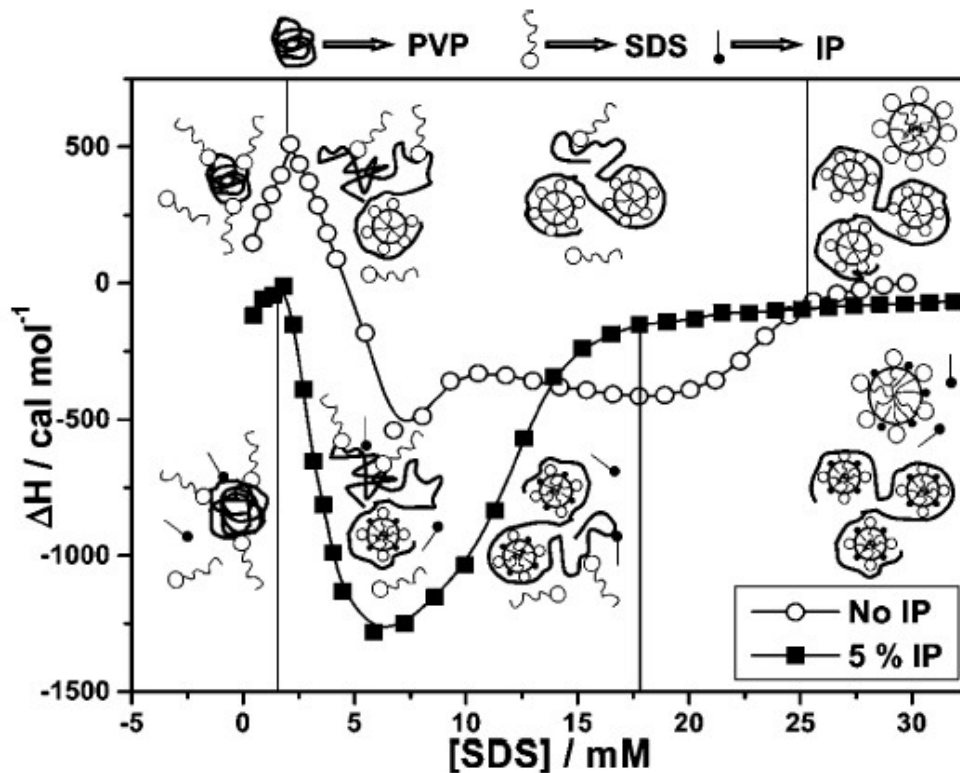
Proposal:

PVP has a significant literature concerning its strong ability to complex anionic surfactants such SDS. I propose that polymerizing NVP in the presence of selected anionic surfactants and RAFT/MADIX CRP(K. Nakabayashi, H. Mori / European Polymer Journal 49 (2013) 2808–2838 is a very detailed review of NVP polymerization

by these techniques) will result in increased tacticity.

Before CRP, NVP free radical polymerization was uncontrolled because the terminal radical is unstabilized and hence very reactive and very short lived. CRP traps the terminal radical and releases it in a controlled slower way. Hence the reformed terminal radical is around longer and with enough time to be effected by its surroundings such as the nature of the solvent or additives.

In researching this idea I discovered that this led me to not only recommend anionic surfactants for tacticity but as agents that would keep the growing pvp chain open and not in a globular state.



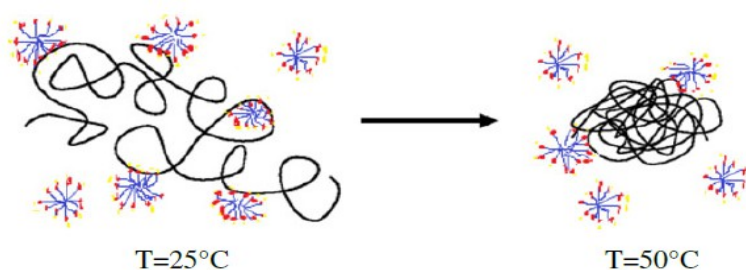
Langmuir 2007, 23, 7531–7538

Interfacial and Bulk Behavior of Sodium Dodecyl Sulfate in Isopropanol–Water and in Isopropanol–Poly(vinylpyrrolidone)–Water Media

Abhijit Dan, Indranil Chakraborty, Soumen Ghosh,* and Satya P. Moulik*

The above chart is similar to several other references. It shows that SDS interacts with PVP in such a way that it swells and makes the terminals much more available. With the right amount of SDS for example NVP would polymerizes to the desired MW with a lower polydispersity because the terminal growing radical would not be buried in a PVP globule, but could continue to add NVP instead of causing a new chain of lower MW to form increasing PD. Temperature is a key parameter.

Scheme 1 Schematic representation of AOT micelles binding into PVP chains



Effect of polymer conformation on polymer-surfactant interaction in salt-free water

Abstract The aim of the present paper was to study the interaction between polyvinylpyrrolidone (PVP) and sodium bis(2-ethylhexyl) sulfoacetate (AOT), as an anionic surfactant, over a temperature range of 25–60 °C by viscosity and electrical conductivity measurements. A coil-to-globule transition of PVP in water was observed. The critical micellar concentration (CMC) was determined by conductivity at 25 and 50 °C. The formation of the complex PVP-AOT in water was studied by conductivity and viscometry at 25 and 50 °C, where the polymer chain adopts respectively coil and globule conformations, and the obtained curves show two break points corresponding to the critical aggregation concentration (CAC) and the polymer saturation point (PSP). The viscometric behavior of PVP-AOT system was studied by using three selected AOT concentrations: $C_{AOT,1}$, $C_{AOT,2}$, and $C_{AOT,3}$ with $C_{AOT,1} < CAC < C_{AOT,2} < PSP < C_{AOT,3}$. For $C_{AOT,1}$, the system behaves as a neutral polymer. A pseudo-polyelectrolyte behavior was observed for the surfactant concentration ($C_{AOT,2}$). Above the PSP, and for the $C_{AOT,3}$ concentration, a screening effect appears due to the increase of the free AOT micelles concentrations. In presence of surfactants, the polymer chains swell especially when the PVP is in globular state.

This paper shows that as the temperature of a PVP solution is increased, the polymer goes from open coil to globule but this effect is reduced in the presence of an anionic surfactants. So you would want to polymerize NVP at the lowest possible temperature in the presence of an anionic surfactant like SDS. This could be done with a redox initiator for example where formation of a free radical initiator does not depend on heat.

Langmuir, 2007, 23 (11), pp 6042–6052

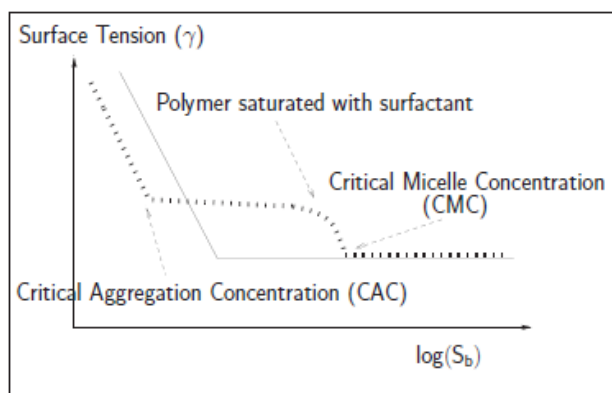


Figure 2: Schematic representation of surface tension against $\log(\text{bulk surfactant concentration})$ for a generic weakly-interacting system. This is represented by the dotted line. The solid line corresponds to a polymer-free solution.

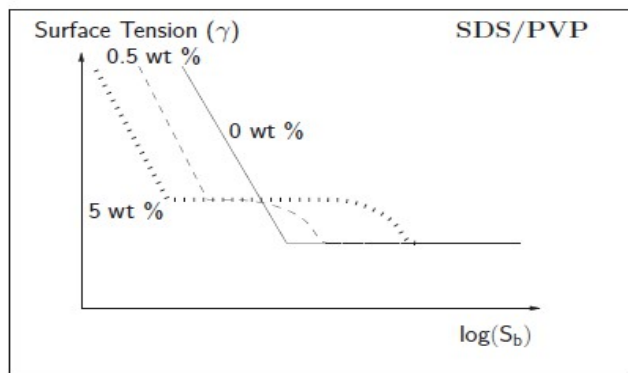
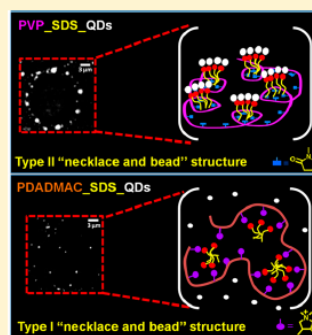
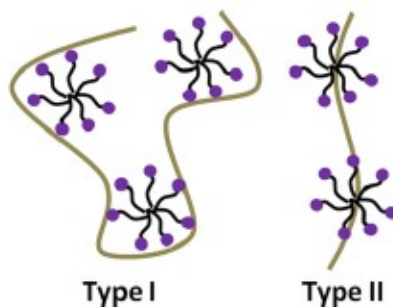


Figure 3: Schematic representation of surface tension against $\log(\text{bulk surfactant concentration})$ for the SDS/PVP system. The three lines correspond to solutions containing 0 wt %, 0.5 wt % and 5 wt % of the polymer PVP.

ABSTRACT: Here, we report the microscopic evidence of “necklace and bead”-like morphology, which has long been the most widely accepted model for polymer–surfactant complexes. The lack of microscopic evidence of the initial complexation between surfactant and polymer has resulted in many contradictory reports in the literature. In this paper, we visualized these initial complexes formed between negatively charged surfactant sodium dodecyl sulfate (SDS) with neutral poly(vinylpyrrolidone) (PVP) and cationic poly-(diallyldimethylammonium chloride) (PDADMAC) polymer through photoluminescence (PL) microscopy and atomic force microscopy (AFM) using silicon quantum dot (Si QD) as an external PL marker. It is observed that, for the PVP–SDS system, SDS molecules bind at the hydrophobic sites on the random-coiled PVP chain through their hydrocarbon tails, while for the PDADMAC–SDS system, SDS head groups are associated with the positively charged nitrogen centers of the polymer, where the polymer chain wraps around the surfactant head groups.



(a) “Necklace and bead”-model



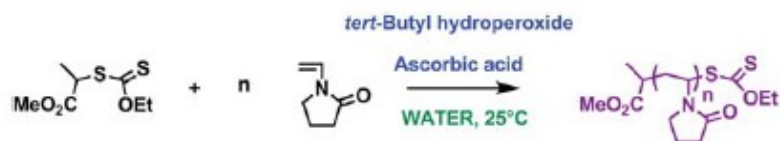
This paper shows that PVP-SDS is a type II complex clearly indicating that my idea of employing a suitable anionic surfactant makes the terminal free radical more available. This is the most recent paper on this subject and sheds a great deal of light on the actual morphology of the complex. The previous papers don't show this as clearly, but support my idea, to polymerize NVP in an aqueous surfactant solution.

Aqueous RAFT/MADIX polymerisation of *N*-vinyl pyrrolidone at ambient temperature†

Aymeric Guinaudeau,^a Stéphane Mazières,^a D. James Wilson^b and Mathias Destarac^{*a}

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DOI: 10.1039/c1py00373a



Scheme 1 Synthetic scheme for redox-initiated RAFT/MADIX polymerisation of *N*-vinyl pyrrolidone in water at ambient temperature.

The above reference, probably the best NVP CRP I have found, clearly shows low temperature CRP with a redox initiator.

Lets say that this idea works and affords PVP with narrower polydispersity and increased tacticity. The remaining problem would be to isolate the polymer without the offending impurities. Polymerization from solid surfaces would work. This is a very active area for LRP (Living Radical Polymerization).

(19) **United States**(12) **Patent Application Publication**
Wang et al.(10) **Pub. No.: US 2016/0024234 A1**
(43) **Pub. Date: Jan. 28, 2016**(54) **NOVEL RAFT AGENTS AND THEIR USE IN
THE DEVELOPMENT OF
POLYVINYLPIRROLIDONE GRAFTED
NANOPARTICLES****Publication Classification**(71) Applicant: **University of South Carolina,**
Columbia, SC (US)(51) **Int. Cl.**
C08F 126/10 (2006.01)
C07D 277/16 (2006.01)
C07D 295/194 (2006.01)(72) Inventors: **Lei Wang,** Columbia, SC (US); **Brian C.
Benicewicz,** Columbia, SC (US)(52) **U.S. Cl.**
CPC **C08F 126/10** (2013.01); **C07D 295/194**
(2013.01); **C07D 277/16** (2013.01)(21) Appl. No.: **14/805,531**(57) **ABSTRACT**(22) Filed: **Jul. 22, 2015**

Nanoparticles having a plurality of PVP chains covalently bonded to a surface of the nanoparticle are provided, along with their methods of formation and the RAFT agents for the polymerization of the PVP chains. RAFT agents are generally provided, along with their methods of formation and use. Methods are also generally provided for grafting a PVP polymer onto a nanoparticle. In one embodiment, the method includes: polymerizing a plurality of monomers in the presence of a RAFT agent to form a polymeric chain covalently bonded to the nanoparticle.

Related U.S. Application Data

(60) Provisional application No. 62/027,510, filed on Jul. 22, 2014.

[BOOK] Controlled Radical Polymerization at and from Solid Surfaces[P Vana, E Bourgeat-Lami - 2015 - Springer](#)

The tailoring of well-defined polymer structures upon the surfaces of solid materials constitutes the molecular basis for advanced functional surfaces. The recent advent of a multitude of controlled radical polymerization methods (also called reversible deactivation ...

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Polymerization of Vac by this method has also been reported:

Macromolecules **2008**, *41*, 7071–7078**Solid-Supported MADIX Polymerization of Vinyl Acetate****Duc H. Nguyen,[†] Murray R. Wood,[‡] Youliang Zhao,^{‡,§} Sébastien Perrier,^{*,‡,||} and Philipp Vana^{*,†}**

Although not completely to my liking because a small amount of unbound polymerization takes place in the solvent phase, the bound polymer is easily recovered and separated. Not only can you make homopolymers, after recovery of the still active particles, other monomers can be added once the solid-supported polymers are placed

back in a suitable solvent.

Apparently the solid-supported catalyst once the attached PVP is removed, could be re-used in subsequent PVP MADIX polymerizations. I want to point out that the solid support can be cellulose with PVP attached to it affording a variety of applications such as grafted PVP-I or PVP-H₂O₂ or biocides and medicinals (*Macromolecules* **2005**, *38*, 10363-10372).

Additional CRP/PVP references:

Macromolecules 2005, *38*, 6770-6774

T. Zhou et al. / *Progress in Materials Science* 83 (2016) 191–235

Macromolecules 2015, *48*, 5459–5469

Chem. Commun., 2013, **49**, 9077—9088

Macromolecules 2009, *42*, 5509–5517

Additional Anionic Surfactant/PVP references:

J. Phys. Chem. B, Vol. 112, No. 12, 2008

Colloid Polym Sci (2014) 292:2485–2495

J. Surf. Interfac. Mater. 1, 77–86, 2013

J Solution Chem (2006) 35:951–968

Summary:

NVP can be polymerized from solid-supported MADIX CTA initiator primed with a small amount of redox generated free radicals and in the presence of an anionic surfactant at an amount near or below the CAC. The low polydispersity PVP can be isolated by recovering the solid-supported MADIX after treatment with, for example, a free radical source. The recovered solid-supported MADIX could be reused in subsequent polymerizations. This would result in a more tactic PVP and a lower polydispersity polymer(copolymer).

Thank you for your interest!

Robert B Login (rloginconsulting.com)