Quantification of Hydroxy Groups on the Surface of Polymer Nanoparticles

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Abstract

Understanding the surface chemistry of particles within a polymer colloid system is crucial for better understanding polymerization processes. A novel method was developed for quantifying hydroxy groups on the surface of polymer nanoparticles. The challenge lay in differentiating surface-region hydroxy groups from those buried within the particle matrix or present in the serum phase. To address this, an aqueous oxidation using silver(II) picolinate was used to selectively convert surface hydroxy groups into ketones without disrupting particle structure. A quantitative NMR approach was envisioned, wherein trimethylsilyl tags were introduced only to non-oxidized hydroxy groups. This approach has shown promising results, allowing for quantification of hydroxy content in the three regions of interest using readily available reagents with minimal sample preparation.

Background

Emulsion polymerization produces a colloid or latex: a stable water suspension of polymer nanoparticles

- Uses in paints, adhesives, cosmetics, drug delivery
- Limits use of volatile organic compounds (VOCs)
- Improves safety on large-scale polymerizations

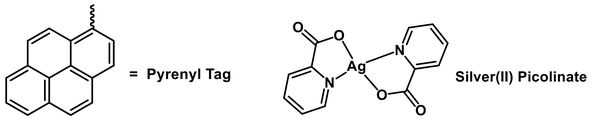
When multiple monomers are used, it is not clear where they end up in the system. Hydroxy groups in particular pose an analytical challenge.

- Particles are easily destabilized, coagulating
- Reactions much be compatible with water, in part

Methods

Fluorescence Spectroscopy

- Relies on the absorption and re-emission of light
- Hydroxy groups can be quantified if fluorescent tags can be added to the surface selectively
- Aqueous oxidation does not affect buried region

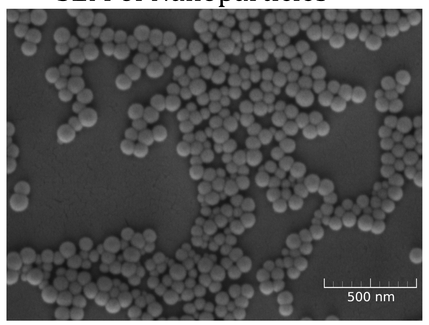


Quantitative Nuclear Magnetic Resonance (qNMR)

- NMR spectroscopy can detect specific nuclei
- Requires an NMR active tag with a strong signal
- Only the non-oxidized hydroxy groups are tagged

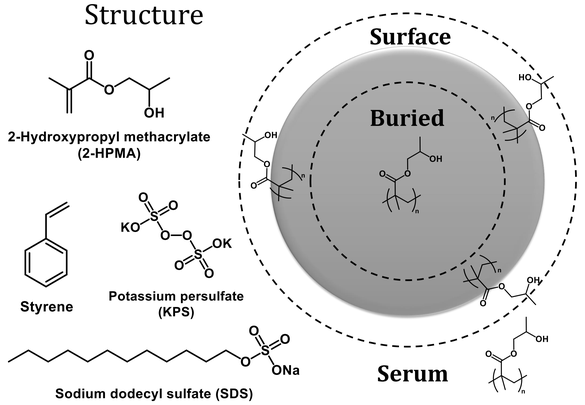
Nanoparticles

SEM of Nanoparticles



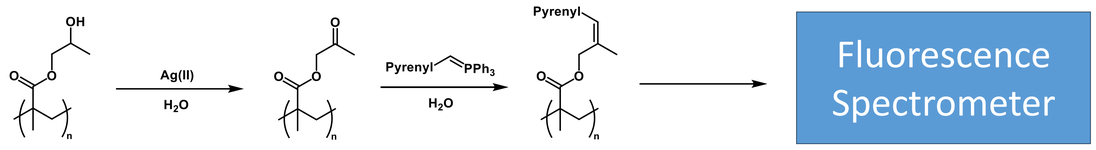
Scanning electron micrograph of the particles used in testing. Taken on TESCAN LYRA3, magnified 89,000x

Structure

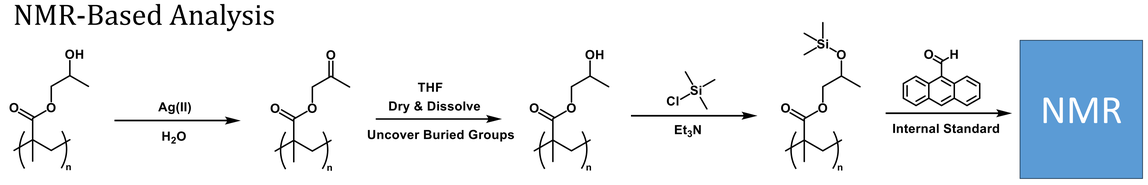


Analysis Process

Fluorescence-Based Analysis

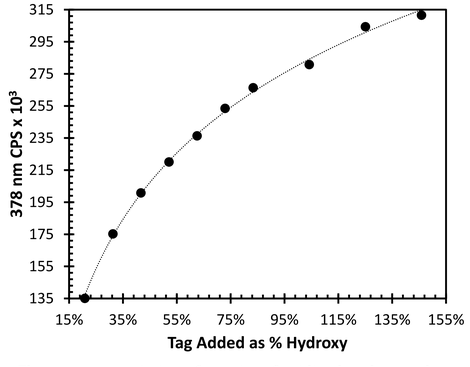


NMR-Based Analysis



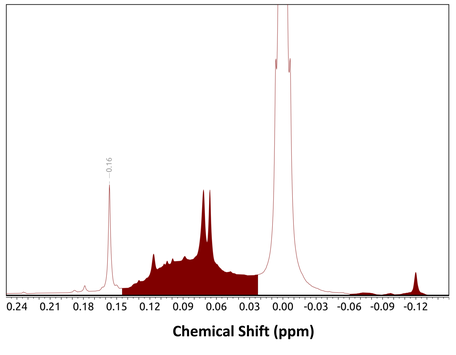
NMR & Fluorescence Data

TD-124 Fluorescence Test



Fluorescence emission of a series of oxidized and tagged particle samples. Dotted line shows a logarithmic relationship.

NMR of Particles



NMR spectrum of isolated, TMS-tagged particles showing the region of interest. Integration gives quantitative data.

Results

Fluorescence Method

- The necessary dual-slope plot was never observed
- Intensity of fluorescence instead increased logarithmically
- No definitive saturation point was determined

qNMR Method

- Non-oxidized latex was analyzed to test efficacy
- 4% 2-HPMA latex was separated by centrifugation
- Serum phase was analyzed on its own
- Particles were oxidized before being analyzed

4% 2-HPMA	Hydroxy Found from Recipe
Total Latex	98.0%
Oxidized Particles	20.8%
Isolated Serum	1.3%

Conclusions & Future Work

- The fluorescence spectroscopy method was found to be ineffective with the tag and conditions used
- The qNMR method returned promising results
- Test on total latex found hydroxy content at 98% of the theoretical amount based on monomer used
- Latex serum and oxidation indicated that 77.9% of 2-HPMA was in the surface region
- Tests need to be repeated on latexes with different monomers and monomer ratios
- Completeness of the oxidation must be verified

Acknowledgements

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