Downscaling of syntheses and preparation of a variety of ^{14}C -labelled polymers and oligomers

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Background

The use of ^{14}C-labelled substances in environmental studies enables the detection of the parent substance, to follow known and unknown transformation products in complex matrices and to establish mass balances in any working step with low effort. While it is a well-established procedure for organic low molar mass compounds e.g. in pesticide regulation, it has rarely been applied for the investigation of the environmental fate of polymers and oligomers, yet. This is mainly due to two principal challenges, first the necessary downscaling to the required small scale synthesis and second the availability of the required ^{14}C-labelled monomers. This often requires creative solutions, some of which we present in the following.

Syntheses – examples

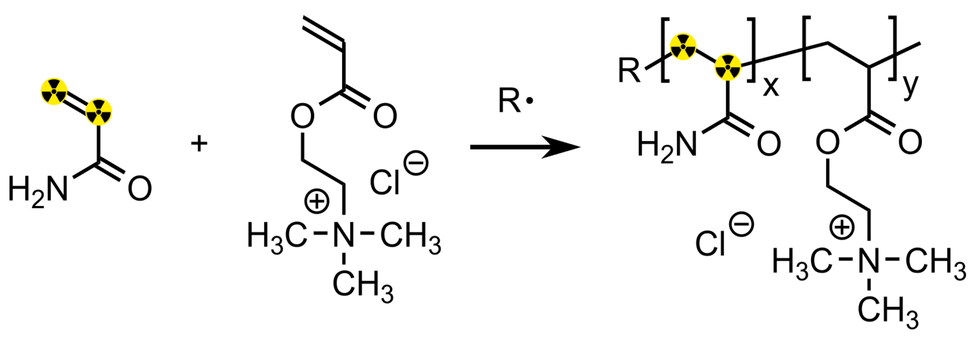
Poly(acrylamide-co-choline acrylate) copolymer

Cationic polyacrylamide-co-choline acrylate copolymer was synthesized using a radical polymerization in aqueous solution.

3 g with a specific activity of ~ 100 kBq/mg were produced and applied in studies according to OECD 307 and 308.

Molecular weight:
^{14}C-Product 3.0 x 10^6 g/mol (GPC-MALS)

^{12}C-reference 3.5 x 10^6 g/mol (Viscosimetry)



Scheme 1: Synthesis of polyacrylamide-co-choline acrylate copolymer

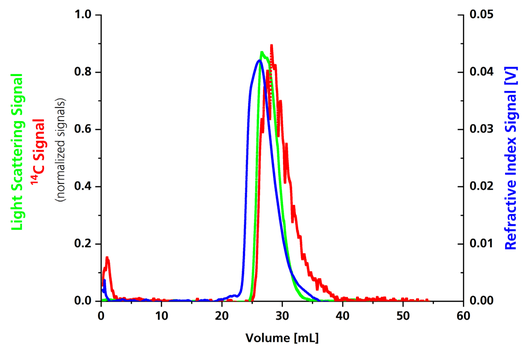


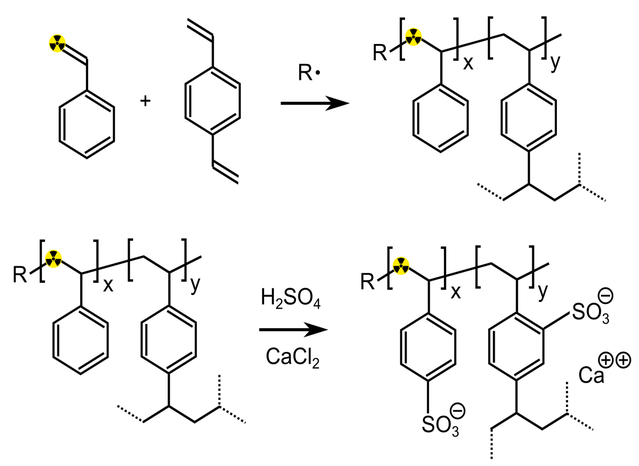
Figure 1: radio-GPC-MALS-RI chromatograms of the final polymer

Calcium polystyrene sulphonate (CaPSS)

Crosslinked polystyrene was synthesized using a suspension polymerization and subsequently sulfonated to form CaPSS.

6 g with a specific activity of ~ 10 kBq/mg were produced and applied in studies according to OECD 303A and 314B.

A main challenge was maintaining a stable suspension in the downscaled approach.



Scheme 2: Synthesis of ^{14}C-labelled Calcium polystyrene sulphonate

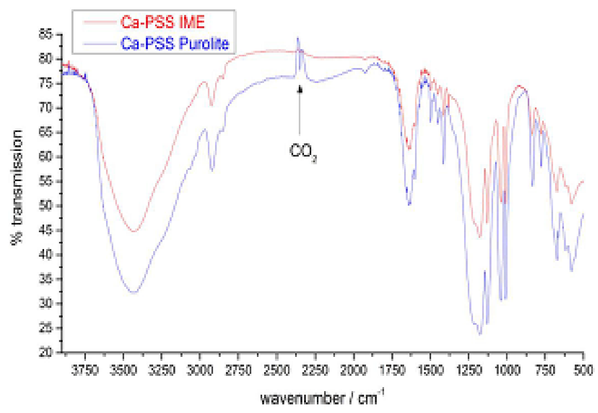
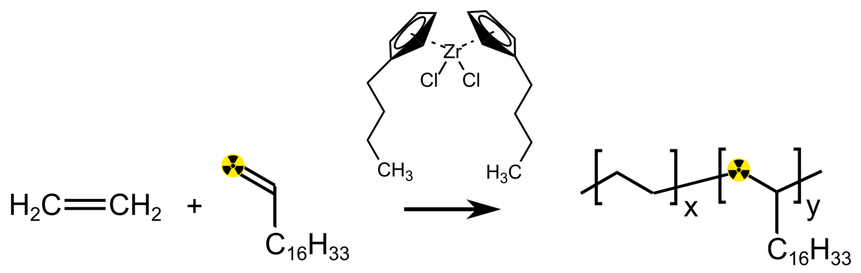


Figure 2: IR-spectra of reference polymer and polymer prepared by downscaled procedure at Fraunhofer IME

Polyethylene

Polyethylene (PE) was synthesized in a Ziegler-Natta type reaction. As no ^{14}C-labelled ethylene is available, the radiolabel was introduced by ^{14}C-labelled octadecene.

5 g with a specific activity of ~ 70 kBq/mg were produced and applied in outdoor lysimeter studies.



Scheme 3: Synthesis of ^{14}C-labelled polyethylene-octadecene copolymer

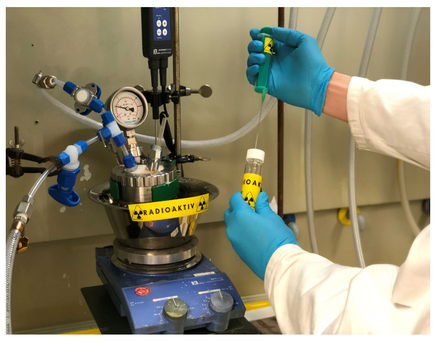
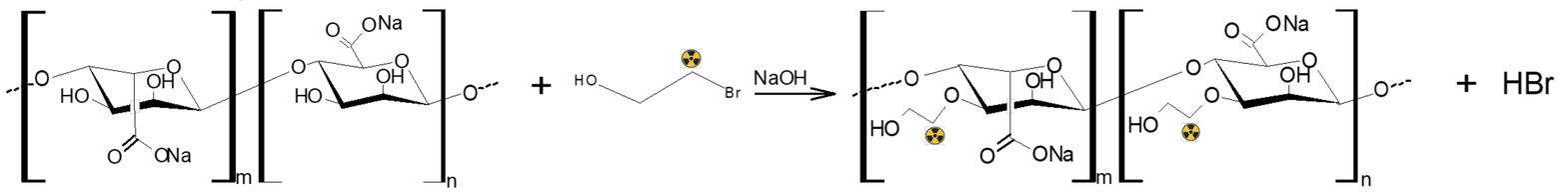


Figure 3: Performance of the ^{14}C-PE synthesis

Outlook: Alginate as example for ^{14}C-labeling of natural polymers

De-novo synthesis of natural polymers is often not possible. However, a post synthetic substitution with a suitable molecule at a considerable low degree will maintain the original properties of the natural polymer. This work is currently in progress.



Scheme 4: Planned synthesis of ^{14}C-labelled alginate

Upcoming: in vivo synthesis of ^{14}C-radiolabelled natural rubber. To be presented in SETAC 2025…