

Polymer and Colloid Highlights

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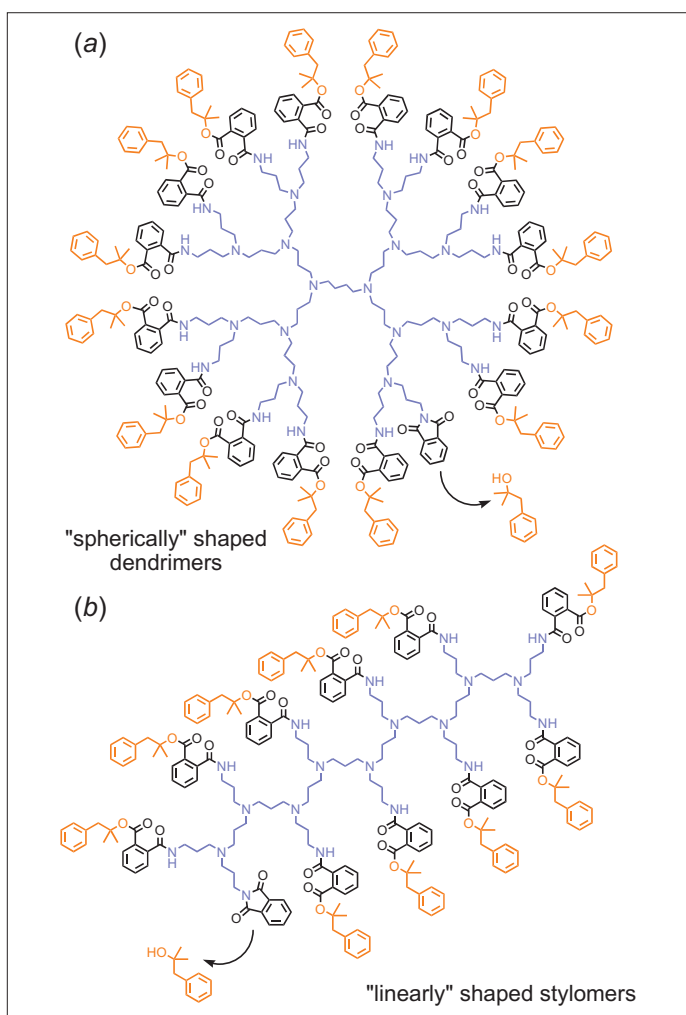
Size isn't Everything! Parameters Influencing the Release of Volatiles from Macromolecular Bioconjugates

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Their unique structures and specific physico-chemical properties make polymers particularly interesting as carriers for the controlled release of bioactive compounds. In particular the



conjugation of volatile fragrance molecules to various different substrates was identified as a powerful tool to enhance the long-lastingness of fragrance evaporation in various practical applications.^[1]

To better understand the parameters governing the release of volatiles from polymeric substrates, we investigated the neighbouring group assisted hydrolysis of 2-carbamoylbenzoates from the surface of 'spherical' dendrimers and 'linear' styloymers serving as model compounds for macromolecular bioconjugates (Fig. 1). Baseline separation of the fully functionalised compounds from their mono-cyclised derivatives by analytical HPLC allowed the determination of the kinetic rate constants for the stepwise cyclisation of the different 2-carbamoylbenzoate moieties.^[2,3]

Our recent studies, carried out at equimolar 2-carbamoylbenzoate concentration in aqueous media at neutral pH and in the presence of a surfactant, showed that the solubility of the bioconjugates had a stronger influence on the rates of hydrolysis than the shape (spherical or linear) or size (generation) of the macromolecules. Additionally, structural features of the local environment near the 2-carbamoylbenzoate release unit, such as the presence of the catalytically active tertiary amine groups in the dendrimer or styloymers backbone, were important for the release efficiency of the bioactive compounds.^[3]

As in high molecular weight polymers the individual monomers are expected to be chemically equivalent, we were interested to see what the minimum size of the macromolecule would be to achieve a constant rate of tertiary alcohol release. Based on the kinetic data measured for the hydrolysis of our series of dendrimers and styloymers, we found that already relatively small structures, in our case a pentakis(2-carbamoylbenzoate) styloymers, marked the transition between 'monomeric' and 'polymeric' behaviour.

To influence the delivery of bioactive compounds from polymer conjugates it is therefore more important to control the physico-chemical parameters in close proximity to the covalent bond cleavage site rather than the macroscopic shape or size of the polymer conjugate.^[3]

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Fig. 1. Controlled release of a tertiary alcohol (in orange) from the surface of dendrimers (a) or styloymers (b, in violet) by neighbouring-group assisted hydrolysis of 2-carbamoylbenzoate moieties (in black).^[3]