

SITE ISOLATION OF FUNCTIONAL CORES USING BRANCHED STAR POLYMERS

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Introduction

In recent years, dendritic backbones¹ have been used extensively for the encapsulation of active core functionalities² and the profound effect of the dendrimer shell on the core properties has been demonstrated. This concept of site isolation³ is of great importance in biomimetics as well as materials science since it allows for creating specific microenvironments around active units.

In order to facilitate the preparation of such functional polymer architectures, we recently developed star polymers having functional cores that can easily be accessed via the ring opening polymerization (ROP) of ϵ -caprolactone using multivalent dendritic initiators.⁴ Here we describe our recent investigations regarding the degree of core isolation in these star polymers as a function of chain length and solvent using a variety of spectroscopic techniques.⁵ The generality and modularity of our synthetic route to achieve efficient core encapsulation have great potential for the design of artificial enzymes and nanoscale devices.

Results and Discussion

Rapid encapsulation of a functional moiety was achieved as outlined in Figure 1 and involves the synthesis of a low generation hydroxyl-terminated aliphatic polyester dendritic initiator⁶ that is capable of undergoing ROP of ϵ -caprolactone.⁷ Polymerizations were carried out in the bulk using catalytic amounts of tin(II) 2-ethylhexanoate.⁸ After single precipitation into methanol the desired polymers were obtained in essentially quantitative yields and narrow polydispersities. In accord with the "living" nature of the polymerization, molecular weights (MW) were easily controlled by adjusting the monomer to initiator ratio.

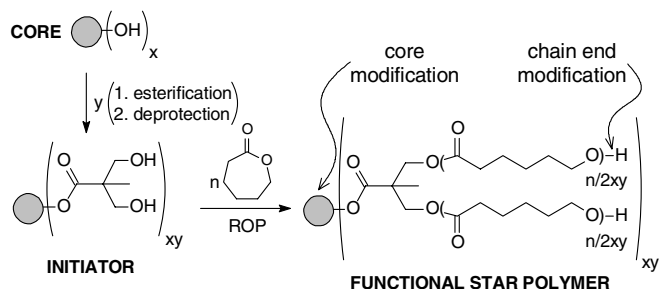


Figure 1. General synthetic realization of core encapsulation involving preparation of the dendritic initiator followed by ROP and postmodification.

In order to elucidate the degree of core isolation we focused on porphyrin and pyrene cores since their unique spectroscopic characteristics allow probing of their microenvironment. The general applicability of the synthetic route and the versatility of the postmodification enabled us to conveniently access three different sets of compounds used in subsequent photophysical investigations (Figure 2). In particular, 2-arm and 4-arm pyrene core stars were prepared for use as solvatochromic probes, 8-arm and 16-arm zinc porphyrin core stars for fluorescence quenching experiments employing external probes, as well as 16-arm coumarin-terminated porphyrin core stars for intramolecular fluorescence resonance energy transfer (FRET) studies.

While the sensitivity of the pyrene core to local polarity differences was decreased by introduction of the ester linkage, fluorescence quenching experiments using methyl viologen as the external quencher were limited to polar solvents. Although a clear increase of site isolation was observed for increasing degrees of polymerization (DP), these methods were not able to simultaneously provide detailed information about both chain length and solvent dependence.

Hence, we chose to explore the facile FRET from coumarin-3-carboxylate donors to the porphyrin acceptor as a sensitive measure for donor (chain end) – acceptor (core) separation and therefore polymer dynamics.

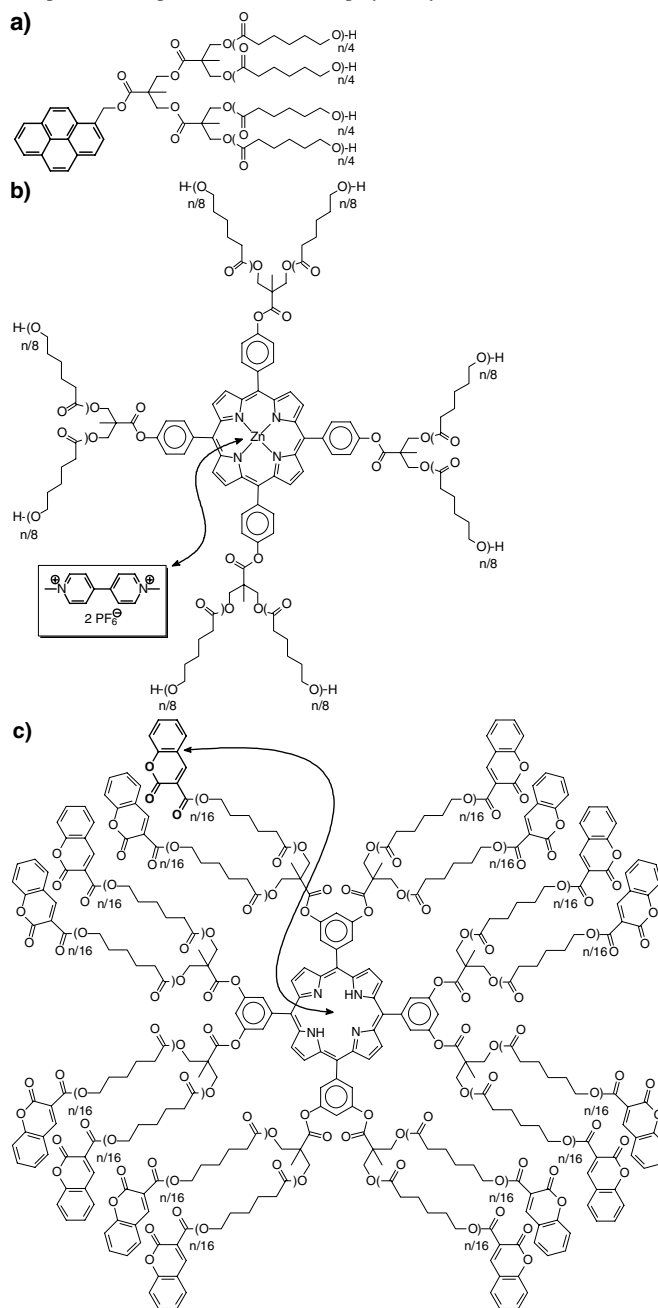


Figure 2. Examples of functional star polymer structures used to investigate core isolation by a) solvatochromic probes, b) intermolecular fluorescence quenching, and c) intramolecular FRET.

Comparing the donor emission in the presence and absence of the acceptor (using a model compound) allowed for the determination of the energy transfer efficiencies (Φ_{FRET}) as a function of chain length, i.e. DP, and solvent (Figure 3).

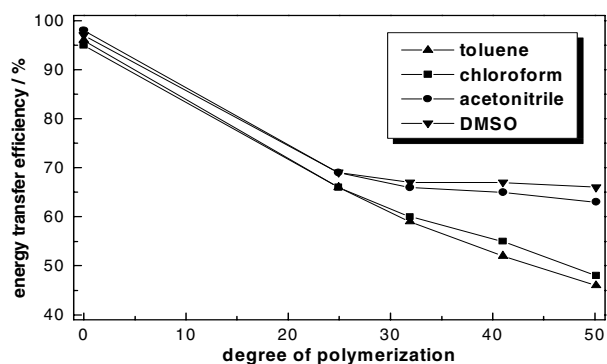


Figure 3. Chain length and solvent dependence of site isolation as determined by FRET (compound Figure 2c).

In accordance to the Stern-Volmer-type fluorescence quenching experiments, increasing core isolation was observed at higher DPs. Additionally, it was found that in poor solvents for the poly(ϵ -caprolactone) backbone Φ_{FRET} is generally higher than in good solvents and that this discrepancy increases with increasing DP. This behavior clearly resembles conformational changes of the polymer backbone. Good solvents lead to extended conformations of the star polymer having a larger *average* donor-acceptor distance compared to the more collapsed structure present in poor solvents (Figure 4).

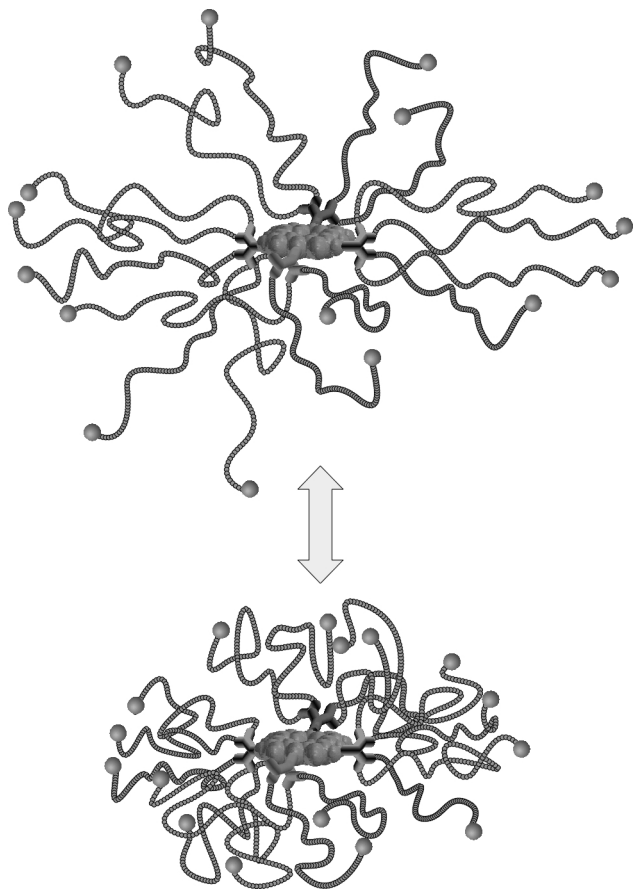


Figure 4. Illustration of solvation induced site isolation showing a more extended conformation of the polymer in a good solvent (top) and its structural collapse in a poor solvent (bottom), therefore leading to enhanced Φ_{FRET} due to a reduced *average* donor-acceptor distance.

The observed solvation-induced encapsulation was independently verified by pulsed field gradient spin echo (PGSE) NMR⁹ experiments that allowed the determination of the hydrodynamic radii (R_{H}). A star polymer (MW = 96500, PDI = 1.10) for instance exhibits $R_{\text{H}} = 9.2$ nm in CDCl_3 but $R_{\text{H}} = 4.6$ nm in CD_3CN . In this particular case ($\Phi_{\text{FRET}} = 50\%$ in CHCl_3), the Förster radius¹⁰ can be calculated ($R_0 = 8.6$ nm) and correlates well with the actual molecular dimensions as obtained by PGSE NMR.

Conclusions

Encapsulation of active cores within branched star polymers via ROP of ϵ -caprolactone using functional dendritic initiators has been demonstrated to be a general and efficient synthetic route. The degree of site isolation has been investigated using various independent spectroscopic techniques and was found to increase with increasing chain length as well as solvent polarity. FRET as well as PGSE NMR have been shown to be particularly useful techniques to study the dynamics of star polymers in solution.

Currently, the above described methodology is used to design nanosized photoreactors, in which light-harvesting antennae systems¹¹ are joined with specifically generated microenvironments to affect chemical transformations.¹²

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