

Synthesis of fluoroalkyl end-capped co-oligomers containing 8-hydroxyquinolyl segments and application to oligomer-catalyzed solvolysis reactions

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Abstract

New fluoroalkyl end-capped co-oligomers containing 8-hydroxyquinolyl segments were prepared by the reactions of fluoroalkyl end-capped co-oligomers bearing isocyanato groups. The solvolysis of *p*-nitrophenyl propanoate (PNP) in the presence of these fluorinated co-oligomers and the corresponding non-fluorinated co-oligomers was investigated in 3:1 (v/v) aqueous methanol buffer solution (0.05 M phosphate, pH 9.2) at 30°C. A large rate enhancement was observed in the presence of the fluorinated co-oligomers for the solvolysis of PNP as compared with the corresponding non-fluorinated co-oligomers. Therefore, these fluoroalkyl end-capped co-oligomers are of particular interest as new fluorinated biomimetic systems for enzyme catalysts. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Fluorinated oligomers; 8-Hydroxyquinolyl segments; Solvolysis; *p*-Nitrophenyl propanoate

1. Introduction

Recently, a great interest has been focused on the synthetic polymer catalysts from the viewpoint of the development of useful and simple model systems for obtaining a better understanding of the origins of enzymatic efficiency and selectivity [1–8]. For example, Fife et al. reported that macromolecules containing the 4-(dialkylamino)pyridine functionality and a bis(trimethylene)disiloxane backbone as a nucleophilic catalyst exhibit enzyme-like substrate selectivity for the solvolysis of *p*-nitrophenyl alkanoates in aqueous and methanol/water solutions [9–14]. On the other hand, we have already reported that organofluorine compounds, especially partially fluoroalkylated macromolecules such as fluoroalkyl end-capped oligomers exhibit various unique properties which cannot be achieved by randomly fluoroalkylated polymers and the corresponding non-fluorinated polymers [15–17]. Of particular interest, our fluoroalkyl end-capped oligomers can easily form molecular

aggregates with the aggregations of end-capped fluoroalkyl segments in oligomers in aqueous and organic media, and these fluorinated aggregates were applied to the molecular recognition of water soluble dyes containing *N,N*-dimethylamino or amino groups such as methylene blue, methyl orange and acriflavine hydrochloride as guest molecules [18]. However, many studies concerning fluoroalkylated polymeric surfactants have not so far been promoted by an interest in modeling enzyme behavior. Therefore, it is very interesting to apply our fluoroalkyl end-capped oligomers to novel fluorinated model systems for attaining the goals of mimicking enzymic efficiency and selectivity. Now, we would like to report on the synthesis of novel fluoroalkyl end-capped co-oligomers containing 8-hydroxyquinolyl segments and in the applications to oligomer-catalyzed solvolysis reactions.

2. Results and discussion

Fluoroalkyl end-capped co-oligomers containing 8-hydroxyquinolyl segments $(R_F-(Qui-OH)_x-(Co-M)_y-R_F)$

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