

Journal of Fluorine Chemistry 107 (2001) 59-62



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

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Received 15 July 2000; accepted 4 September 2000

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 propaonate (PNP) in the presence of these fluorinated co-oligomers and the corresponding – 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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Scheme 1.



Scheme 2.

 $R_F = CF(CF_3)OCF_2CF(CF_3)OC_3F_7)$ were prepared by the reactions of 5-amino-8-hydroxyquinoline (AQui–OH) with the corresponding isocyanate co-oligomers $(R_F-(IMBO)_{x}-(Co-M)_{y}-R_F)$ in which the reactive isocyanate moieties were protected as 2-butanone oxime adducts according to our recently reported method [19]¹ as shown in the following Scheme 1.

The fluorinated co-oligomers thus obtained were slightly soluble in water; however, they were easily soluble in MeOH, EtOH, THF, chloroform and DMSO. Therefore, these fluorinated co-oligomers are applicable to new fluorinated surfactant catalysts.

A typical solvolysis study was performed as follows. Solvolysis reactions were followed from the absorbance of the p-nitrophenoxide anion at 400 nm in aqueous methanol buffer as shown in Scheme 2.

The sample cuvette was filled with 3.0 ml of a fresh solution containing fluoroalkylated co-oligomers in a 3:1 (v/v) aqueous methanol buffer solution (0.05 M phosphate, pH 9.2), and the solution was equilibrated for 2 h at 30°C. A solution (12 ml) of *p*-nitrophenyl propanoate (PNP) in dioxane was added by microsyringe. The reaction mixture was mixed quickly by shaking, and absorbance at 400 nm was recorded as a function of time.

Fig. 1 shows the appearance of the *p*-nitrophenoxide ion in the solvolysis of PNP with R_{F} -(Qui–OH)_x-(DMAA)_y- R_{F} (see Scheme 1) and the corresponding non-fluorinated cooligomer: –(Qui–OH)_x–(DMAA)_y– as a function of time. An unmeasurably rapid increase ("burst") is followed by slow linear increase, which can be derived into the apparent firstorder solvolysis of PNP. In the absence of co-oligomers, the solvolysis of PNP catalyzed by aqueous methanol buffer solution shows no burst of *p*-nitrophenoxide, and followed an apparent first order equation. Interestingly, a more rapid increase was observed in the case of R_{F} –(Qui–OH)_x– (DMAA)_y– R_{F} compared to the corresponding non-fluorinated co-oligomer. The magnitude of the initial burst was proportional to the concentration of the co-oligomer as shown in Fig. 2.

The rate constant $(k_{\rm sp} = 1.98 \times 10^{-4} \text{ s}^{-1})$ of PNP solvolysis in the absence of co-oligomers was found to be similar to the values for $k_{\rm sp}$ (PNP) (data not shown) of

¹A typical experiment for the synthesis of R_F-(Qui-OH)_x-(DMAA)_y- $R_F [R_F = CF(CF_3)OCF_2CF(CF_3)OC_3F_7]$ is as follows: perfluoro-2,5dimethyl-3,6-dioxanonanoyl peroxide (2.5 mmol) in 1:1 mixed solvents (AK-225) of 1,1-dichloro-2,2,3,3,3-pentafluoropropane-1,3-dichloro-1,2,2,3,3-pentafluoropropane (30 g) was added to a mixture of isocyanatoethyl methacrylate 2-butanone oxime adduct (2.5 mmol), N,N-dimethylacrylamide (DMAA: 25 mmol) and AK-225 (100 g). The solutions was stirred at 45°C for 5 h under nitrogen. After evaporating the solvent, the crude products were reprecipiated from methanol-hexane to give R_F- $(IMBO)_x - (DMAA)_y - R_F [R_F = CF(CF_3)OCF_2CF(CF_3)OC_3F_7] (3.64 g,$ Mn = 1640). A solution of the obtained co-oligomer [0.6 mmol (1.01 g)] and 5-amino-8-hydroxyquinoline (AQui-OH: 1.2 mmol) in DMF (10 g) was stirred at 120°C for 1 h. After evaporating the solvent under reduced pressure, the crude products were reprecipitated from chloroform-hexane to give R_F -(Qui-OH)_x-(DMAA)_y- R_F [R_F = CF(CF₃)OCF₂CF(C-₂CF(CF₃)OC₃F₇; 0.84 g]. This cooligomer showed the following spectral data: IR v (cm⁻¹) 3450 (OH), 1720, 1631 (C=O), 1320 (CF₃), 1248 (CF₂); ¹H NMR (CDCl₃) δ 0.78-3.20 (CH₂, CH, CH₃), 3.31-4.29 (CH₂), 6.78-9.03 (5H); ¹⁹F NMR (CDCl₃, ext. CF₃CO₂H) δ -4.21 to -7.95 (26F), -54.00 (6F), -69.95 (2F); average molar mass $(M_n) = 4920$ $(M_w/$ $M_{\rm n} = 1.20$; x:y = 12:88). Molecular weight and co-oligomerization ratio were determined by gel permeation chromatography (GPC: calibrated with standard polystyrenes by using tetrahydrofuran as the eluent) and ¹H NMR, respectively.



Fig. 1. Time dependence of the liberation (absorption (λ_{max} : 400 nm)) of *p*-nitrophenoxide in the solvolysis of PNP (166 μ M) catalyzed by fluorinated and non-fluorinated Qui–OH–DMAA co-oligomers. (\bigcirc) R_F– (Qui–OH)_x–(DMAA)_y–R_F ($M_n = 4920$ ($M_w/M_n = 1.20$; x:y = 12:88; concentration of oligomer: 140 μ M); (\bigcirc) –(Qui–OH)_x–(DMAA)_y–($M_n = 6580$ ($M_w/M_n = 1.13$); x:y = 11.89; concentration of oligomer: 140 μ M); (\triangle) no oligomer.



Fig. 2. Relationship between the concentration of Qui–OH monomer unit in co-oligomers and the absorbance released in the burst stage of *p*nitrophenoxide ion (λ_{max} : 400 nm), (\odot) R_F–(Qui–OH)_x–(DMAA)_y–R_F ($M_n = 4920 (M_w/M_n = 1.20)$; *x*:y = 12:88); (\bigcirc) –(Qui–OH)_x–(DMAA)_y– ($Mn = 6580 (M_w/M_n = 1.13)$; *x*:y = 11:89).

PNP solvolysis after the burst release of *p*-nitrophenoxide anion in each concentration of the co-oligomer as shown in Fig. 1 and Scheme 3.

Similar results were obtained in the solvolysis of PNP with R_F -(Qui-OH)_x-(ACMO)_y- R_F ($M_n = 2820$ (M_w /

 $M_n = 2.16$); x:y = 17:83) (see Scheme 1) and -(Qui-OH)_x-(ACMO)_y- ($M_n = 8430$ ($M_w/M_n = 1.38$); x:y = 5:95) (see Scheme 1), and a more rapid increase in the burst stage was observed in the case of the fluorinated ACMO co-oligomer. These findings suggest Qui-O⁻ anions in co-oligomers could react quantitatively with PNP within a few seconds as shown in the burst stage (k_a in Scheme 3), and PNP could undergo solvolysis (k_{sp} (PNP)) catalyzed by aqueous methanol buffer after the burst process. We can easily calculate the yield of the solvolysis product (*p*-nitrophenol: $\varepsilon = 18180$) of PNP from the slope of Fig. 2, and the yields are as follows:

	Yield of <i>p</i> -nitrophenol $(\%)^{a}$
R_{F} -(Qui-OH) _x -(DMAA) _y - R_{F}	14
-(Qui-OH) _x -(DMAA) _y -	6

^a Yield is based on the Qui–OH monomer unit in cooligomers.

From these results, it was clear that fluoroalkyl endcapped co-oligomers are more reactive (2-3 times) than the corresponding non-fluorinated co-oligomers. Additionally, ACMO co-oligomers (yield of p-nitrophenol: 43% (fluorinated co-oligomer); 19% (non-fluorinated co-oligomer)) were more reactive than the corresponding DMAA cooligomers. This would depend upon the fact that ACMO cooligomers are likely to form the more hydrophobic microdomains. In general, it is well known that hydrocarbon polysoaps are not likely to form molecular aggregates in aqueous solutions, and there should be entanglement between polysoaps in aqueous solutions [20,21]. Therefore, Qui-OH segments in non-fluorinated co-oligomers could interact slightly with PNP, and PNP could exist in the partially constructed hydrophobic microdomains. In contrast, fluorinated co-oligomers should easily form molecular aggregates with aggregations of end-capped fluoroalkyl segments. Thus, our present fluorinated co-oligomer aggregates can provide very favorably hydrophobic microdomains. In such suitable microdomains, Qui-O⁻ anions in fluorinated co-oligomers could interact very effectively with PNP to suffer an acyl transfer reaction from PNP, resembling a biomimetic system for enzyme catalysts such as α-chymotrypsin.



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